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INDUSTRIAL CHEMICALS SOLID WASTE GENERATION
THE SIGNIFICANCE OF PROCESS CHANGE, RESOURCE RECOVERY, AND IMPROVED DISPOSAL

J. C. Saxton, et al

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The study characterizes the process-related solid wastes produced during manufacture of industrial chemicals, SIC Group 281. Thirty three chemicals were selected that: possess significant resource value, pose a difficult solid waste disposal problem, and/or have markedly deleterious properties, e.g., toxicity. The selected chemicals composed 40% of 1971 group output (149 x 10^6 tons) and an estimated 95% of the group's solid waste. Fifteen of the chemicals are undergoing process substitutions; in every case the newer process generates less solid waste.

Projection to 1977 indicates that process and raw material changes reduce the overall solid waste quantity 7.3%. Most of wastes are of intrinsically low value, so resource recovery is seldom economic. Inorganics account for over 90% of total disposal cost, due to large waste volume from ore-related processes, such as alumina and phosphoric acid. Organics appear to pose little disposal problem. Elimination of water discharge doubles the disposal cost of the 33 chemicals.

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WASHINGTON, D.C. 20460

ABSTRACT

The objective of the study was to characterize the process-related solid wastes produced during the manufacture of industrial chemicals, SIC Group 281. Thirty three chemicals were identified that suffice to represent the entire Group in terms of solid waste generation. The criteria for selection were that the resulting solid waste: possess significant resource value, pose a difficult waste disposal problem, and/or have markedly deleterious propoerties, e.g., toxicity. The presence of toxic components is particularly significant in that they inhibit resource recovery and necessitate greater care and expense in disposal. The selected chemicals composed 40% of the 1971 Group output (149 x 10^6 tons), and are estimated to account for over 95% of the Group's solid waste.

Factors leading to a change in solid waste generation include: market growth or decline, process substitutions, process modifications, and raw material changes. The latter refers to those cases in which the production process remains essentially unchanged even though the raw materials change, e.g., ore grades. Fifteen of the 33 selected chemicals were found to be undergoing process substitutions, and in every case the newer process generates less solid waste. A five year projection to 1977 indicates that process and raw material changes reduce the overall solid waste quantity 7.3%, and if phosphorus and phosphoric acid are excluded, the reduction is 13.6%.

The resource value of the solid waste stream from the 33 chemicals, if all contained chemicals could be sold at market value, is 11.9% of the $7.2 billion production value of the primary chemicals. Most of these resources are of low value, however, and cannot compete in the commercial market. A case study of sodium sulfate illustrates the way in which the supply of a ubiquitous byproduct increases beyond its market demand. Another case study, of phosphorus and phosphoric acid, depicts a situation in which a scarce resource (fluorine) is presently discarded with process waste. In this instance, resource recovery is important, even though the waste volume is not reduced thereby.

Disposal costs were estimated for the solid wastes from each of the 33 chemicals. Inorganics account for over 90% of the total cost, with Industry 2819 alone accounting for more than 71%. The latter is due to the large waste volume from the ore-related processes, such as alumina and phosphoric acid. In terms of disposal, the organics appear to pose little problem. The elimination of water discharge as a disposal alternative was found to double the disposal cost of the 33 chemicals.

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I. CONCLUSIONS

The findings of this study are that:

(1) ongoing process substitutions are acting to produce a significant reduction in quantity of wastes generated--by 1977, process substitutions will reduce solid wastes from the selected chemicals by 7.3%;

(2) the viability of resource recovery as a method of waste reduction is hampered in Sector 281 by the intrinsically low economic value of most waste materials produced;

(3) constraints on disposal of solid wastes to water bodies are already being translated into economic decisions by the industry.

These findings lead us to conclude that the emphasis of Federal action should be upon the promulgation of environmentally based regulations for solid waste disposal. Action is presently being undertaken in the areas of sanitary landfill and hazardous waste disposal. Similar steps should be taken for disposal via lagoons and subsurface injection. In each case, an important aspect is the establishment of a monitoring and data assessment system to evaluate the immediate and long term effects of the disposal method. Subsurface injection monitoring is particularly critical due to the difficulty in correcting the situation if leakage develops. In all modes the significance of even small quantities of toxic material must be carefully assessed.

II. RECOMMENDATIONS

This study has developed the context within which more detailed assessments of resource recovery and waste disposal can be carried out. In addition, our method of evaluation of the effect of process substitution on pollutant generation can be fruitfully extended from solid wastes to air and water borne wastes. Specifically, we recommend:

(1) an equivalent assessment of the effect of process substitution on the air and water borne wastes from Sector 281;

(2) the extension of such analysis to all wastes from other large waste producing economic sectors;

(3) the identification of the flow paths of valuable materials, such as scarce metals, through Sector 281, starting with their purchase by that sector; then an evaluation of the potential for recovery of these materials at that point at which they enter the waste stream;

(4) a regional analysis of the synergistic effect of use and generation of hazardous materials by contiguous industries;

(5) a detailed economic study of the waste handling alternatives, including resource recovery, for the more burdensome wastes, such as those from phosphoric acid;

(6) the placing of documentation requirements on the producers of solid waste, such that the quantity and chemical composition of the waste generated at each production facility is identified.

III. INTRODUCTION

PROJECT SCOPE

This project has considered:

- The amount and composition of the solid wastes generated during industrial chemicals manufacture;
- The present means for handling and disposing of these wastes;
- The manner in which these wastes evolve with time due to process substitutions and modifications;
- The opportunities for resource recovery and/or improved treatment and disposal of these wastes; and
- The governmental strategy options for affecting solid waste management in the industrial chemicals sector.

Industrial chemicals manufacture forms Sector 281 in the Standard Industrial Classification; included are the following six major subgroups:

2812	Alkalies and Chlorine
2813	Industrial Gases
2815	Cyclic Crudes and Intermediates, Dyes, and Organic Pigments
2816	Inorganic Pigments
2818	Industrial Organic Chemicals, NEC*
2819	Industrial Inorganic Chemicals, NEC*

In 1970 industrial chemicals were manufactured at 2034 plants employing 252,200 people.[1] The value of shipments in that year was $14.3 billion, which represents over one-third that of the entire Chemicals and Allied Products Major Group (#28).

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*NEC, Not Elsewhere Classified.

The wastes generated at an industrial chemical production facility are of two distinct types: process related and non-process related. The latter are those wastes generated in any production facility that are due to 'overhead' activities not directly attributable to the production process. For example, cafeteria trash, sewage, used computer paper, etc., are all in the latter classification.* The former, on the other hand, relate directly to the primary production process. If plant output is increased, these wastes are also generated in proportionally greater measure. This study has considered only process related wastes, and has further restricted its attention to those wastes unique to the chemical industry. Thus, proper management of flyash from power generation and activated sludge from waste water treatment has not been addressed. On the other hand, liquid/solid mixtures, such as slurries and sludges, have been included because they are inherently associated with the production process and are often handled together with dry solid wastes.

PROJECT OBJECTIVES

The purpose of the present investigation was four-fold:

(1) to delineate the extent and nature of the solid wastes generated during industrial chemicals manufacture in sufficient detail that the significance of these wastes to the nations economy and environment can be properly appraised;

(2) to assemble a data base appropriate to an evaluation of the potential for and importance of resource recovery from industrial chemical solid wastes; to consider a number of examples illustrating the dimensions of the resource recovery opportunities associated with industrial chemical solid wastes;

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*These do not usually contain toxic or hazardous materials.

(3) to identify present waste disposal practices in the industry and to indicate areas in which this practice could or should be improved; and

(4) in line with the foregoing, to consider the appropriateness of alternative courses of governmental action in the development of sound solid waste management practices for the industrial chemicals group.

PROJECT BACKGROUND

The IR&T study is a follow-on to a prior study of industrial chemical solid wastes by The Research Company (TRC) of New England. That work was sponsored by the Industrial and Agricultural Data Section, Division of Technical Operations, EPA National Environmental Research Center, Cincinnati, Ohio. The TRC report titled, "Solid Waste Management in the Industrial Chemical Industry,"[2] was completed in early 1971. TRC considered both process and non-process wastes.

TRC grouped process wastes in six categories:

(1) sludges,
(2) filter residues,
(3) tars,
(4) flyash,
(5) off-quality product, and
(6) all other.

Using a survey technique, TRC gathered data on the generation of these various waste types within the industrial chemical industry. They also explored the methods employed for solid waste management and described the production processes for a number of representative chemicals, including a discussion of the sources of solid waste generation and general nature of the resulting waste.

While the TRC study offers a useful orientation regarding the general nature of industrial chemical solid wastes, it is not helpful in identifying areas for potential resource recovery. Nor does it offer insight into the manner in which the solid waste streams can be expected to change in the future. For both these purposes it is necessary to identify the specific waste streams from each process, in terms of quantity and chemical composition. Knowing the stream content and the geographic location of its generation, it is possible to speculate on the potential for resource recovery. Knowing the manner in which the production processes are evolving, it is possible to determine the changing character of the overall industrial solid waste output, including toxid hazards.*

Another factor that has played a role in shaping the form of the IR&T study is an extensive investigation of the treatment and disposal of hazardous chemicals undertaken by EPA. This investigation was conducted in compliance with Section 212 of the Resource Recovery Act of 1970. That act dictated that a technologic and economic evaluation be carried out regarding the establishment of a system of National Disposal Sites for hazardous wastes. Over 1.5 million dollars has been expended by five contractors** to develop a data base describing toxic wastes generation; explore resource recovery, treatment, and disposal options; conduct economic assessments of a system of National Disposal Sites and of alternative approaches; and survey citizen opinions regarding community acceptance of a Disposal Site. IR&T has incorporated relevant findings of the hazardous waste effort into this study, and, where appropriate, we have adjusted the direction of our effort to avoid an unproductive overlap of the two studies. For example, less emphasis was placed on waste treatment and disposal than originally planned, while the manner in which the waste stream is evolving received greater emphasis.

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*Data of the type assembled by TRC is somewhat helpful in overall consideration of treatment and alternate disposal requirements. Even here, however, specific characterization of the waste streams is necessary before detailed evaluations can be undertaken. Toxic hazards were not considered.

**Booz Allen Applied Research Inc.; TRW, Battelle Memorial Institute, Pacific Northwest Laboratories; Arthur D. Little Inc.; and HumRRO.

Although the hazardous waste effort forms an important complement to the IR&T study, there are significant differences between the two efforts. Our study focuses on the whole range of process-generated solid wastes unique to the industrial chemical industry, whereas the hazardous waste study considers only toxic wastes, while encompassing all industrial sources and including air and water pollutants in addition to solid wastes. (In fact, 90% of the toxic wastes were found to be water borne.) In extending beyond toxic wastes, IR&T considered those solid wastes that contain significant resource value or pose difficult treatment/disposal problems.

PROJECT METHODOLOGY

The conduct of the project can be described in terms of six consecutive phases:

(1) develop data base for present solid waste quantities and chemical composition;

(2) identify present solid waste management practice for selected wastes;

(3) identify ongoing or planned industrial process changes and assess their effect on the solid waste stream;

(4) evaluate potential for resource recovery from candidate waste streams;

(5) explore alternatives for improved waste treatment and disposal; and

(6) utilize the foregoing information to assess governmental strategy options for influencing industrial chemical solid waste management.

In the following sections each phase is discussed in terms of the principal decisions affecting the structure and content of this study.

Develop Data Base

The initial phase of the project involved selecting representative chemicals from among the several thousand inorganic and organic chemicals produced by the industrial chemicals sector. A manageable subset of representative chemicals was needed to characterize the sector as a whole in terms of its solid waste stream. The criteria for selection arise naturally from the objective of the study, namely to identify needs and opportunities for improved waste resource recovery, treatment, and ultimate disposal. To qualify for inclusion on the list, the waste chemicals had to satisfy the following requirements, viz.

(1) possess significant resource value,

(2) pose a difficult waste disposal problem, and/or

(3) have markedly deleterious properties, e.g., toxicity, combustibility.

Using these criteria, 33 specific chemicals were chosen to provide a reasonable characteristic sample of the entire sector. These 33 chemicals accounted for 40% of the 149 million short tons of product output by Sector 281 in 1971. In terms of solid waste, we estimate that production of the selected chemicals accounts for more than 95% of the entire sector's solid waste. The emphasis of the present study was not specifically upon toxic wastes. Since some of the smaller production processes may contribute a disproportionate share of the toxic waste, a follow up to the present study which focus upon toxic wastes is in order.

Having selected the chemicals to be studied, initial estimates for the solid wastes from each were refined. In doing so, information was obtained from the published literature [3, 4, 5],* EPA publications and data [6-12], Bureau of Mines data [13, 14] trade associations, industrial concerns**, and IR&T industrial process files. From these diverse data sources, estimates were made and cross checked for the solid wastes generated by each production process. Then, the participation of each process in the production of the marketed chemical was determined from SRI data [15], published information***, and trade association information. Knowing the participation of each process and its associated solid waste, the overall solid waste associable with each chemical and with the entire set of 33 chemicals was directly determined.

Appraise Present Solid Waste Management

The nature of the solid waste treatment presently afforded the 33 representative chemicals was identified via literature search, plant visits, and discussions with governmental and industrial representatives. The costs of such treatment were estimated based on knowledge of the waste composition and rough guidelines for such costs as furnished in the literature. The emphasis in this portion of the study was to formulate an approximate, but consistent, estimate of solid waste management costs. This information was then used as a point of departure for the consideration of improved disposal.

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*The published literature contains primarily process information. Waste data must be calculated or inferred. References 3 to 5 are the primary texts employed. Other references are given in the subsequent discussion of the solid waste data base.

**Dr. Joan Berkowitz of Arthur D. Little, who was working on a companion study to establish a solid waste classification system, was of particular assistance. She arranged for IR&T staff to discuss our project with those Arthur D. Little Staff members familiar with the chemicals of interest.

***Individual sources employed are referenced in the chapter on the solid wastes data base.

Assess Change in Solid Waste Stream

The amount of solid waste generated by production of a specific chemical varies with time. There are four major determining influences: market growth or decline, process substitutions, process modifications, and raw material changes.* In overall terms, the market for industrial chemicals has been continually expanding since the construction of a sulfuric acid plant in Philadelphia in 1793. From 1958 to 1967 value added by manufacture in the Chemical and Allied Products Sector (SIC Sector 28) grew by 90%, and that of Industrial Chemicals (Sector 281) by 83.5%.[16] Superimposed on the overall growth, however, competition among chemicals led to a decline in demand for some chemicals and an accelerated growth for others. For example, since 1945 ethylene has progressively displaced acetylene in nearly all applications. In the four-year period from 1964 to 1968 annual production of ethylene increased by 52% as contrasted with a minor 8.6% increase in acetylene production.[17]

Process substitution relates to the competition between alternative production processes for a given chemical. Benzene offers an interesting illustration of this type of substitution. Benzene was originally produced as a byproduct of steel manufacture. Coal tars given off during the production of coke were distilled to produce a number of chemical products, including benzene, toluene, xylene, and butadiene. Such products, called coal tar derivatives, are included in SIC Sectors 2815 and 2818. Since the mid 50's, however, benzene and the other coal derivatives have been produced in increasing quantity with petroleum as feedstock.* Today, 90% of benzene is produced from petroleum, and this feedstock continues to increase its share of the market. Coal tar production of benzene actually declined 22.2% from 1964 to 1968[18]. As production shifts from one process to the other, the amount and nature of the solid wastes produced correspondingly shift. (As it happens, petroleum based production of benzene is classified in SIC Sector 2911, and so is not included within the purview of our study.**) In the case of benzene, it is anticipated that with the advent of large scale coal conversion processes in 1987[19], or so, that coal will again offer a competitive alternative to petroleum as a benzene feedstock, and hence another change to the solid waste stream will occur.

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*Raw material changes could be considered within the general category of process changes. We discuss them separately because frequently the process operations remain the same, even though the raw material may change. An example is the processing of various grades of ore.

The third major factor acting to produce a change in the solid waste stream is process modification. The principal modifications affecting solid waste generation are: changing the process operating conditions, adding process steps for resource recovery and general waste reduction, and upgrading process air and water pollution control capability. The first two modifications tend to reduce the solid waste load while the last tends to increase it. Examples of changing the process operating conditions without changing the basic process include: changing reaction temperature or pressure; replacement of a fixed by a fluidized bed; increasing the amount of material recycled to the reactor; introducing on-line process computer control; or replacing the present catalyst with another that allows higher or lower temperature operation, increases reaction rates, or is easier to regenerate. Such process changes are normally introduced in order to increase yield, and therefore are judged on an economic basis.* An accompanying benefit, however, is that the process waste load is usually concurrently reduced as process efficiency increases. Because of its economic significance, information regarding the details of process modifications is frequently regarded as proprietary.

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*In this case the process substitution is related directly to a raw material change. There are distinct differences between the processes utilizing the two feedstocks, however. We consider Category 4 - raw material-related changes to solid wastes generation - to apply to those situations in which the process remains essentially unchanged, e.g., a change in ore grade.

**If coal tars are not used in the production of benzene and other chemical products, they will presumably be burned. They then pose a waste disposal problem attributable to steel production (Sector 3313).

Process modification via the addition of process steps for resource recovery and general waste reduction is in fact the focus of our study. Such additional steps can be carried out either at the production facility, by an independent processor, or at a municipal facility such as a National Disposal Site (whether privately or governmentally operated). In all cases, the waste is presently being disposed of in some way, so these additional steps represent an upgrading of the solid waste management process.

Another type of process modification affecting the solid waste stream is the transformation of air and water borne wastes into solid wastes. This transformation is already underway due to recent legislation, and will come to nearly complete fruition over the next decade and a half.

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*Environmental regulations will play an increasing role in all process modifications (and initial process designs or selections) as these regulations are translated into economic terms and hence are accounted for in process management decisions.

The amount of material so transformed will increase as the legislative constraints on air and water pollution tighten. By 1977 "best practicable technology" will be required for water treatment, and by 1983 the standards will be raised to "best available technology" with the express goal of reaching zero discharge. In effect, all pollutants now released into the air and water will eventually be treated as solid wastes unless otherwise eliminated by the factors discussed above, e.g., process substitution and/or modification.

The last major factor to be considered regarding solid waste generation is the selection and treatment of raw materials (without process change). This factor may lead to either an increase or decrease in process solid wastes. On the one hand, for political, economic, or environmental reasons, raw materials of lower grade, such as some types of domestic ores, may take the place of higher grade feedstocks, and these lower grade materials will impose a greater solid waste burden. On the other hand, higher grade materials may become available or raw materials may be more highly beneficiated at the mining (or extraction) site. It should be noted that the pretreatment of raw materials is directly equivalent to adding later process steps, merely occurring as a precursor rather than a postcursor to the process. The solid waste load is shifted from the production facility to an earlier stage (and location) in the materials conversion sequence.

It is revealing to consider the significance of resource recovery in light of the foregoing discussion. That is, the need for and nature of the additional process steps must be interpreted within the context of overall market considerations, ongoing technological substitutions, and modifications of existing processes introduced to achieve greater efficiency. The economic leverage of each of these three factors is considerably greater in most instances than that offered by increased recovery of resource value or otherwise optimum disposal of the waste.

Only legislative constraints can rearrange these relative priorities. For this reason a great deal of emphasis was placed in our study on identification of the trends in regard to market and process technology and interpretation of their significance to solid waste generation. Three case studies were conducted to illustrate these considerations.

In order to develop a framework within which the need for and nature of additional process steps for resource recovery and improved treatment/disposal can be evaluated, the solid wastes attributable to the 33 selected chemicals were projected forward five and ten years. In doing this, account was taken of market considerations, process substitutions, and process modifications. Least-squares fits to historical time trends and specific knowledge of industrial plans were employed in making the projections. Greater knowledge of actual industry capacity expansion plans would permit increased accuracy in this projection, of course, but it is felt that a reasonable and meaningful projection has been achieved. The legislative factors affecting air and water pollutant contributions were reviewed, but quantitative evaluation of these contributions was beyond the scope of this study.

Consider Need and Potential for Resource Recovery

The need for resource recovery was addressed within the context of the resource value presently discarded through existing waste management practice. It was considered of central importance to determine whether scarce resources are being dissipated. An upper limit estimate was made for the commercial value of the wastes from each of the 33 chemicals based on the market value of the contained chemicals. Present market size was used as a gauge of the ability of the commercial market to absorb the waste chemical if recovered. A case study was made of the possibility for resource recovery from the wastes of the two chemicals-phosphorus and phosphoric acid - which together generate more solid waste than the other 31 chemicals combined.

Explore Needs and Capabilities for Improved Treatment and Disposal

To reiterate, the principal mode for improved disposal is to adjust the production process in such a manner as to reduce the amount of solid waste generated. Once this is done, the most significant problem associated with the solid waste load is that of toxicity. The detailed studies of hazardous waste disposal recently made under EPA sponsorship were reviewed in terms of their applicability to the industrial chemicals sector. Aspects of present disposal practice for the 33 representative chemicals that require modification were identified and potential alternative approaches indicated. Estimates were made of the revised disposal costs. The demands on land use were considered within the context of the present waste load and that projected for 1977. It was assumed that little ocean dumping or subsurface injection will be practiced in 1977.

Assess Governmental Strategy Options

The emphasis in our approach was to determine whether there are areas in which governmental action would be clearly beneficial. The alternatives for governmental action considered were:

(1) regulation,
(2) tax incentives,
(3) subsidy,
(4) preferential procurement,
(5) research and development, and
(6) public education.

In approaching the study it was assumed that economic self-interest of the industry will, in nearly all cases, operate to encourage resource recovery and waste reduction. The study sought to identify marginal instances in which additional incentive or disincentive may produce a desirable change, yet will not disrupt the industry. Alternative governmental actions were evaluated using such criteria as: the importance of the problem, the size and character of the alleviation government action would accomplish, its cost, what sector would bear the cost, whether disruption to the industry would result, and the time required to accomplish the change.

IV. INDUSTRIAL CHEMICAL SOLID WASTE GENERATION

In this chapter we consider the mechanisms for generation of process solid waste and the types of waste that result. Using the criteria described previously, a subset of representative chemicals that characterize the solid wastes of SIC Sector 281 is identified.

SOLID WASTE ORIGINS AND CHARACTER

Within the category of solid waste (as we have defined it for purposes of this study) are materials ranging from slurries to dry solid cake; from combustible organic tars to inert inorganic salts; from toxic materials, such as chromates, to common salt. These wastes arise from three principal sources:

(1) unreacted raw materials,
(2) contaminants of the raw materials, or
(3) by-products of the chemical reaction.*

The contribution from unreacted inputs can be expressed in terms of overall reaction yield: a yield of 80% means that 20% of the limiting reactant and a somewhat greater percentage of the other reactants remain unconverted. By-products, the third category, can be further differentiated into coproducts of the main reaction or products of an undesired side reaction. An example of the latter is NO_x generation in combustion processes. Again, not all of the wastes will be solid wastes. However, even airborne and waterborne wastes may be subsequently converted to solid form, i.e., in the course of air and water treatment. Hence, particulates and water-soluble salts are considered here with other solid wastes.

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*To some extent the principal product also enters the waste stream as a result of inadequate separation. It may appear as a solid waste.

An example of a solid waste traceable to material entering in the raw material stream is shown in Figure 1.[20] This figure depicts the processing sequence for the manufacture of benzene, toluene, and xylene (BTX) from coal tars. In this process the crude oil contaminants are separated from the desired products by acid washing and alkali neutralization. An acid and an alkali sludge result. Subsequently, the desired products are mutually separated by fractional distillation, and the still bottoms are removed as waste tars.

A primary distinction between the chemicals composing Sector 281 is whether they are organic or inorganic. For the most part the solid wastes associated with the two chemical types are quite different. The BTX example considered above is interesting because it is an exception to the general rule. For the most part, the production of organic chemicals involves the use of a petroleum feedstock whose contaminants have been stripped away during the prior refining process (SIC Sector 2911). In this event the principal solid wastes from production of the organic product are organic tars formed as undesired products of side reactions. These tars may be furthur stripped of chemical value by subsequent processes. For example, one of the alternatives for production of carbon tetrachloride and perchloroethylene is called the "garbage can" process because it accepts waste tars formed during earlier chlorination steps. In effect, this process serves as a resource recovery step. Alternatively, waste tars can be incinerated with or without heat recovery. For the most part, disposal of organic tars is not difficult, however, the cost of incinerating corrosive halogen-containing tars is significant, and frequently leads to their disposal through landfill.

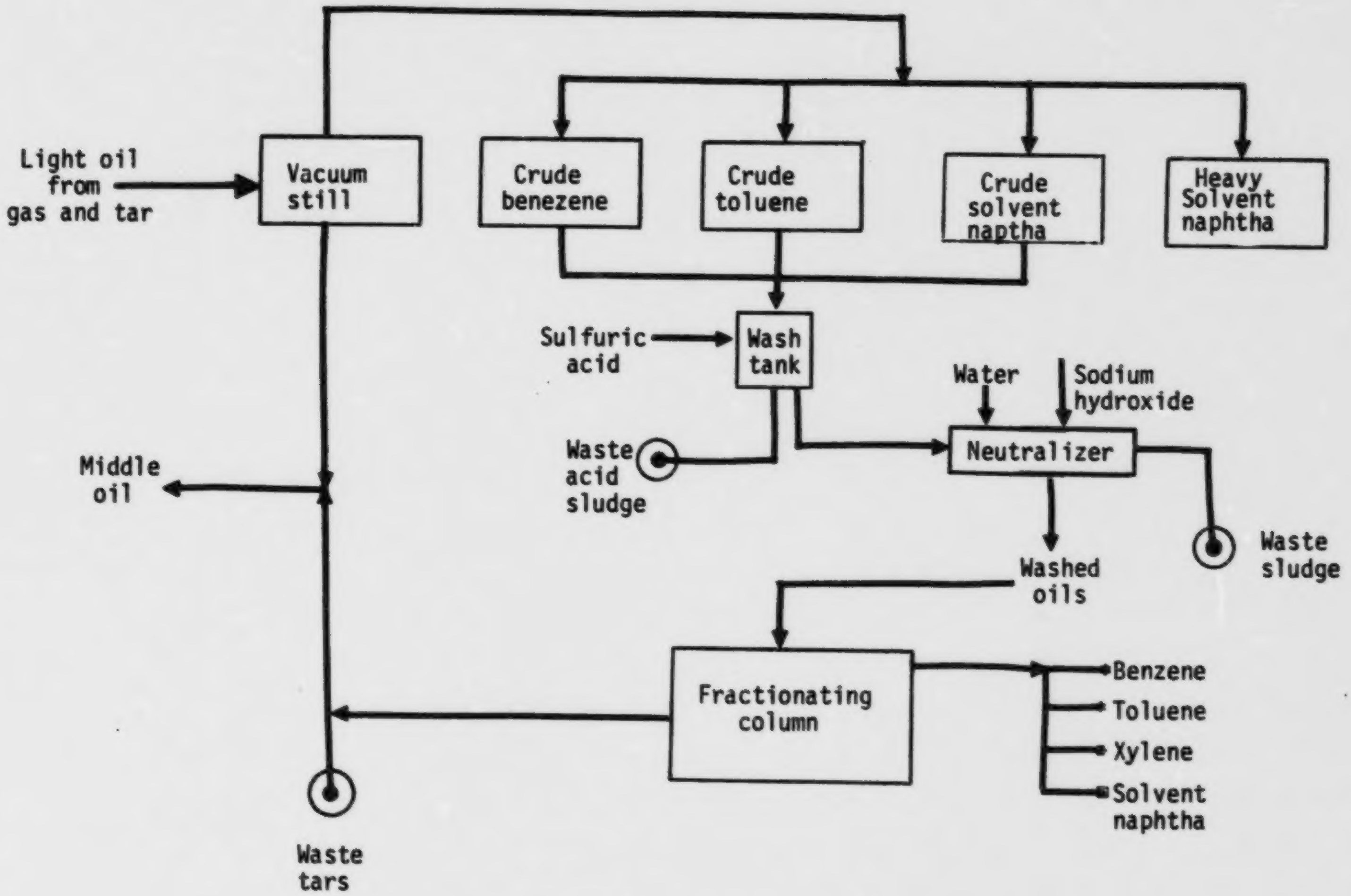
Light oil from gas and tar
Vacuum still
Crude benezene
Crude toluene
Crude solvent naptha
Heavy Solvent naphtha
Sulfuric acid
Wash tank
Waste acid sludge
Water
Sodium hydroxide
Neutralizer
Waste sludge
Middle oil
Washed oils
Fractionating column
Benzene
Toluene
Xylene
Solvent naphtha
Waste tars

Figure 1. Manufacture of toluene, benzene, and xylene from coal tar light oil by acid washing. Reference 2.

Spent catalysts are an important component of the solid waste from organic chemical production. These materials are of interest due to their metallic content and because they are frequently of a toxic nature. They were not studied in detail during this project because we found the chemical industry fully aware of their resource value, and acting accordingly. For example, spent nickel catalysts are conventionally shipped to Europe for their metallic value there,[21] and Union Carbide sells spent catalyst from phthalic anhydride production for its vanadium content.[22]

The BTX example represents a deviation from the general rule that the raw materials for organic chemicals are relatively uncontaminated. In this instance, the production process is one step closer to the initial step in the materials processing sequence than is normally the case for organic chemicals. The processes by which chemicals are produced occur on a number of levels, the first being the beneficiation of the extracted ore or refinement of the basic oil or gas. Only the raw materials associated with the initial conversion steps carry unwanted material with them.

As a more typical example, consider phosphate rock processing. Phosphate rock is washed at the mining site to remove material undesired in later processing steps.* The resulting sand tailings and phosphate slurries (classified here as solid waste) account for sixty-eight percent of the weight of the mined rock, or 2.1 lbs. waste per lb. product. The slime is a particularly voluminous and undesirable waste having a low solids content ($\simeq$5%) which settles out very slowly over a period of years. At the next stage in materials conversion, phosphoric acid is produced. The earlier beneficiation step greatly reduces the waste that would otherwise be attributable to phosphoric acid production.* Nevertheless, a certain amount of mineral contaminants are given off as sludge waste, 0.21 lbs/lb product. The use of phosphoric acid in subsequent processing steps, such as fertilizer production or sugar refining, entails essentially no ore-related solid wastes.

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*The beneficiation of phosphate rock falls within SIC Sector 1475.

Although there are ore-related wastes involved in phosphoric acid production, the principal solid waste from the "wet process" is an economically undesired coproduct--calcium sulfate dihydrate or "gypsum"--produced in the main chemical reaction. The "wet process" sequence is shown in Figure 2.[23] The chemical reaction, with 95% yield, is:

$$Ca_{10}F_2\ (PO_4)_6 + 10H_2SO_4 + 20\ H_2O \rightarrow 10CaSO_4 + 20H_2O + 2HF + 6H_3PO_4$$

In this reaction, 3.36 lb of gypsum is produced for every lb of phosphoric acid. The gypsum is separated through filtration, and normally is sent to lagoons for temporary storage with later release to a river body during periods of high flow. The gypsum is "discarded" in this manner because in the United States gypsum from natural deposits is available in abundant quantity and at low price. Thus, whether gypsum--like many other coproducts--is a desired material or a waste is a question of geochemistry and economics.

For the most part, the nature of the waste relates to its origin and those generated by inorganics differ from those output from organic reactions. Raw-material-related wastes and undesired coproducts are generally attributable to inorganic reactions. Tars (by definition) and spent catalysts can usually be related to organic reactions. In

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*The discussion here pertains to the "wet process" for phosphoric acid manufacture. In the dry process, the phosphate rock is employed directly, without prior beneficiation.

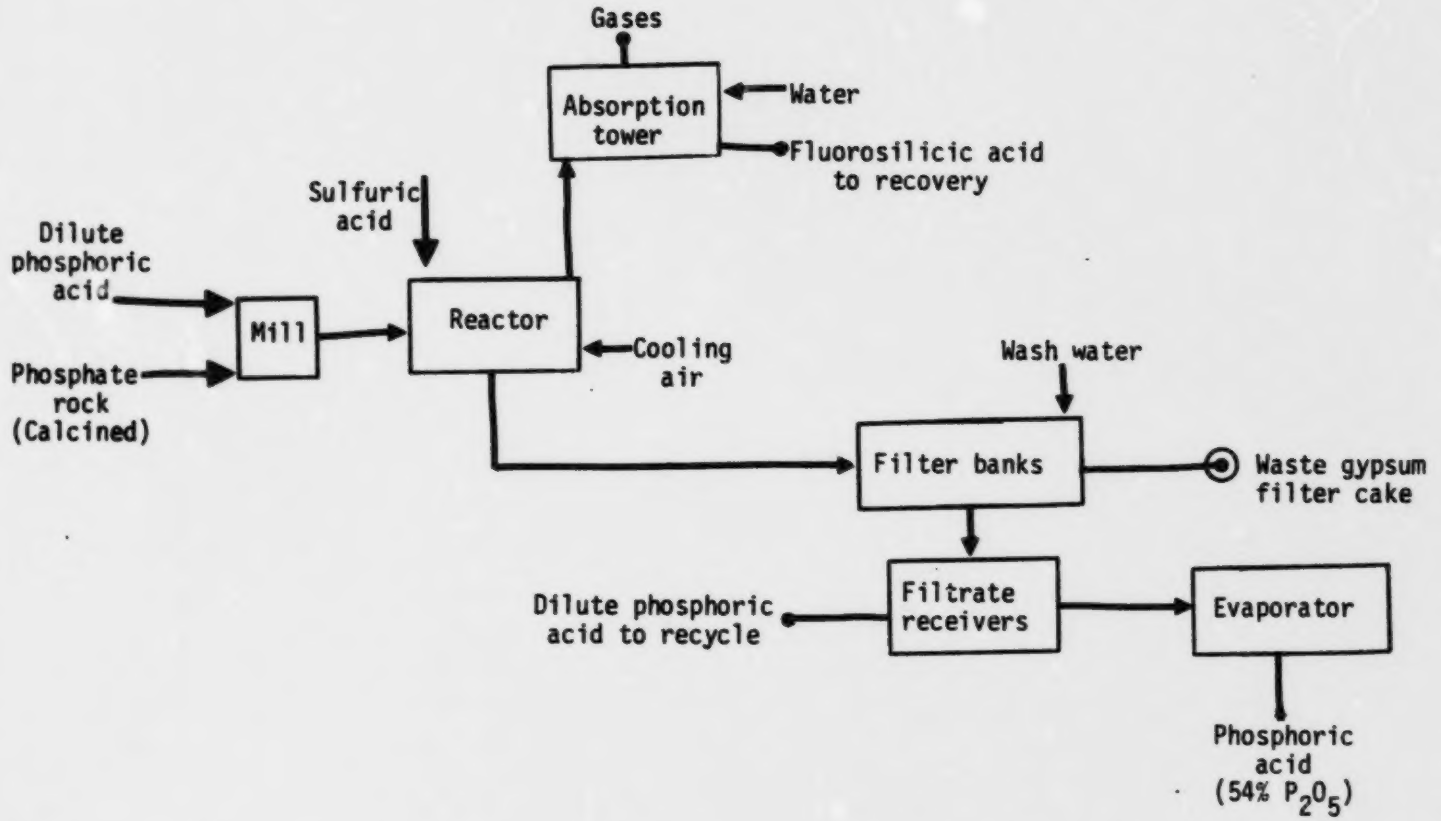
Gases
Absorption tower
Water
Fluorosilicic acid to recovery
Sulfuric acid
Dilute phosphoric acid
Mill
Reactor
Phosphate rock (Calcined)
Cooling air
Wash water
Filter banks
Waste gypsum filter cake
Filtrate receivers
Evaporator
Dilute phosphoric acid to recycle
Phosphoric acid (54% P_2O_5)

Figure 2. Manufacture of phosphoric acid from phosphate rock by the wet process. Reference 2.

the following section, a subset of representative chemicals are selected in order to permit specific consideration of the options available in industrial chemical solid waste management.

SELECTION OF REPRESENTATIVE CHEMICALS

As stated in the introduction, the principal criteria employed in selecting representative chemicals to characterize Sector 281's solid waste load were that the waste:

(1) possess significant resource value,
(2) pose a difficult waste disposal problem, or
(3) have markedly deleterious properties, e.g., toxicity.

There were also a number of secondary criteria employed in order to achieve general balance in our selections. These secondary criteria were that:

(4) at least one representative be considered from each SIC 281 subgroup,
(5) a roughly equivalent number of inorganic and organic chemicals be included, and
(6) all of the leading commercial chemicals from 281* be considered as candidates.

We will now discuss the manner in which these criteria were utilized in the selection process, and identify the chemicals selected.

Roughly 200 production processes associated with industrial chemical manufacture were reviewed from the perspective of their production of solid wastes. The level of detail employed is exemplified by standard chemical engineering reference works, e.g., Faith, Keyes, and Clark[24] and Kirk and Othmer.[25] Inorganic reactions were examined for production of a non-economic coproduct, use of crude raw materials, or low reaction yields. Organic reactions were primarily examined for low reaction yield. In addition, EPA reports[26-28] on the industries of interest were reviewed. An initial designation of toxic wastes was made based on the process review. The estimates for toxic waste loads were later correlated with those made in the concurrent EPA study of hazardous wastes.[29-32] The solid wastes associated with mineral ores were checked against information presented in Bureau of Mines publications.[33,34] On the basis of such an assessment and extension of available literature, fifty-two chemicals were initially selected. Following discussions with industry personnel and our own appraisal of the relative significance of wastes, fifteen chemicals were dropped from further consideration leading to a final subset of 33 chemicals, of which 16 are inorganic and 17 are inorganic. These are listed by SIC category in Table 1.* Their solid wastes are felt to be sufficiently representative of the Sector 281 solid waste load as to permit the formulation of meaningful conclusions regarding proper solid waste management for the entire sector. In Table 2 the selected chemicals are delineated in terms of the mechanism by which they generate solid wastes and the criteria under which they were chosen. In the following paragraphs, examples are given that illustrate use of the various selection criteria.

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*In terms of value of shipments.

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* All chemicals and groups of chemicals contained in Sector 281 are given in Table A1 of the Appendix.

TABLE 1

SIGNIFICANT SOLID WASTE PRODUCERS AMONG INDUSTRIAL CHEMICALS

(Grouped by Standard Industrial Classification Category)

281 Industrial Inorganic and Organic Chemicals

2812 Alkalies and Chlorine

Chlorine
Sodium carbonate (soda ash)
Sodium hydroxide (caustic soda)

2813 Industrial Gases

Acetylene

2815 Cyclic Intermediates, Dyes, Organic Pigments, and Cyclic Crudes

Aniline
Benzene
Benzene hexachloride
Chlorobenzene
Phenol
Phthalic Anhydride
Styrene

2816 Inorganic Pigments

Titanium dioxide
Zinc oxide

2818 Industrial Organic Chemicals, Not Elsewhere Classified

Chloroform
Ethylene dichloride
Ethylene glycol
Ethylene oxide
Formic acid
Glycerine
Perchloroethylene
Propylene oxide
Tetraethyl and tetramethyl lead

TABLE 1 (contd.)

2819 Industrial Inorganic Chemicals, Not Elsewhere Classified

- Aluminum oxide (alumina)
- Aluminum sulfate
- Ammonium chloride
- Boric acid
- Chromium trioxide (chromic acid)
- Hydrochloric acid
- Hydrofluoric acid
- Phosphorus
- Phosphoric acid
- Sodium chromate and dichromate
- Sodium sulfite

TABLE 2

CHEMICALS SELECTION CRITERIA AND SOLID WASTE ORIGIN

SIC SECTOR	SECTOR TITLE	CHEMICAL	INORG.	ORG.	SW ORIGIN			SELECTION CRITERIA		
					RM CONTAMINANT	BYPRODUCT	SIDE REACTION	RESOURCE VALUE	DISPOSAL* PROBLEMS	DELETERIOUS** PROPERTY
2812	Alkalies Chlorine	Chlorine }	✓		✓			✓	✓	✓
		Sodium Hydroxide }								
		Sodium Carbonate	✓							
2813	Industrial Gases	Acetylene	✓			✓			✓	
2815	Cyclic Intermediates..	Aniline^{+}		✓		✓	✓		✓	
		Benzene		✓			✓		✓	
		Benzene Hexachloride		✓			✓			✓
		Chlorobenzene		✓			✓			✓
		Phenol		✓		✓	✓		✓	✓
		Phthalic Anhydride		✓			✓	✓		
		Styrene		✓			✓		✓	
2816	Inorganic Pigments	Titanium Dioxide	✓		✓			✓	✓	
		Zinc oxide	✓		✓				✓	
2818	Industrial Organic Chemicals NEC	Chloroform^{+}		✓		✓	✓		✓	
		Ethylene Dichloride		✓					✓	✓
		Ethylene Oxide } $^{+}$		✓		✓			✓	
		Ethylene glycol }								
		Formic Acid		✓		✓			✓	
		Glycerine		✓		✓	✓		✓	
		Perchloroethylene		✓		✓	✓			✓
		Propylene oxide		✓		✓			✓	
		TML/TEL		✓	✓				✓	✓

TABLE 2 (cont'd)
CHEMICALS SELECTION CRITERIA AND SOLID WASTE ORIGIN

SIC SECTOR	SECTOR TITLE	CHEMICAL	INORG.	ORG.	SW ORIGIN			SELECTION CRITERIA		
					RM CONTAMINANT	BYPRODUCT	SIDE REACTION	RESOURCE VALUE	DISPOSAL* PROBLEMS	DELETERIOUS** PROPERTY
2819	Inorganic Chemicals NEC	Alumina	✓		✓			✓	✓	
		Aluminum Sulfate	✓		✓			✓	✓	
		Ammonium Chloride	✓			✓			✓	
		Boric Acid	✓		✓				✓	
		Chromium Trioxide	✓		✓				✓	
		Hydrochloric Acid	✓			✓			✓	
		Hydrofluoric Acid	✓		✓				✓	
		Phosphoric Acid	✓		✓			✓	✓	
		Phosphorus	✓		✓				✓	
		Sodium Chromate + dichromate	✓		✓				✓	✓
		Sodium Sulfate	✓			✓			✓	

*Large volume wastes included within this criteria.

**Chlorinated tars are included within this criteria.

+The older processes fit the checked criteria. In the case of aniline and ethylene oxide the older processes have been completely eliminated, and in the case of chloroform the older process has been almost entirely eliminated.

TABLE 3

CHARACTERIZATION OF PRINCIPAL CHEMICAL'S PRODUCTION

SIC	PRINCIPAL CHEMICAL	ANNUAL PRODUCTION Y-1971 MM.S.T. /YR.	UNIT VALUE (¢/lb)	RANK * (1969)	ANNUAL GROWTH 1961 - 1971	# COS	# Plt.	# St.	% BY TOP 4	MAJOR PROCESS ALTERNATIVE	PROC. %	COMPANY	PROCESS	GEOGRAPHIC LOCATION (STATE)	CAPACITY (MM.S.T. PER YEAR)
2816	Zinc Oxide	.220	16	IO-26	3.5%	16	18	10		American Process from ore and residual (AP)	60.0	Am Zinc Co[4]		Oh/Ill	
												Anaconda[4]		Mont	
										French Process from zinc metal (FP)	28.3	Cities Svc Co[4]		Tenn	
										Other	11.7	Dia Sham[4]		Penn	
2818	Chloroform	.119	17.25	OI-69	11.6%	6	9	8	91.5	Chlorinating Methene (CM)	95	Dow	CM	Tx/La	0.080
												Stauffer	CM	Ky	0.038
										Acetone & Bleaching Powder (AB)	5	Allied	CM	SC	0.015
												Dia. Sham	CM	SC	0.007
2818	Ethylene Dichloride	3.58	9	OI-5	18%	12	16	4	59.1	Ethylene and Chlorine (EC)	100	Shell	E/C	Tx	0.85
												PPG	E/C	La/P.R.	0.842
												Dow	E/C	Tx/La	0.800
												Dia. Sham	E/C	Tx	0.595
2818	Ethylene Oxide	1.81	7	OI-3	10%	14	28	8	64.3	Direct Oxidation (DO)	89.2	Union Carb	DO	SC/P.R./Tx/La/ Calif	0.660
												Dow	CH/DO	Tx/La	0.500
	(Ethylene Glycol)[2]	(1.51)	(8.5)	(OE-24)						Chlorohydrin[3] (CH)	10.8	Jefferson Chem	DO	Tx	0.350
												PPG	DO	P.R./Tx	0.190

TABLE 3 (cont'd).

CHARACTERIZATION OF PRINCIPAL CHEMICAL'S PRODUCTION

SIC	PRINCIPAL CHEMICAL	ANNUAL PRODUCTION Y-1971 MM.S.T. /YR.	UNIT VALUE (¢/lb)	RANK * (1969)	ANNUAL GROWTH 1961 - 1971	# COS	# Plt.	# St.	% BY TOP 4	MAJOR PROCESS ALTERNATIVE	PROC. %	COMPANY	PROCESS	GEOGRAPHIC LOCATION (STATE)	CAPACITY (MM.S.T. PER YEAR)
2818	Formic Acid	.009 (1963)	13			3	6	4	100	Sodium Formate (SF)	30^{6}	Dupont		NJ	0.007
												Sunoco		SC/NJ	0.0035
										By-product and Others (BP)	70^{6}	Union Carbide	BP	Tx	0.015
2818	Glycerine	.167	13-24		0.5%	3^{7}	4^{7}	2^{7}	100^{7}	Synthetic	70.7				
										a. Allyl Chloride (AC)	51.8	Dow^{7}	AC	Tx	0.060
										b. Propylene Oxide (PO)	8.4	FMC Corp^{7}	PO	Tx	0.020
										c. Acrolein (A)	10.5	Shell^{7}	A	Tx/La	0.087
										Natural	29.3				
2818	Perchloro-ethylene	.351	10.25	OE-58	12%	8	13	8	73.2	Chlorination of hydrocarbons (CH)	94	Dia. Sham	CH	Tx	0.100
												Dow Chem	CH	Tx/Cal/La	0.085
										Acetylene & chlorine via trichloro ethylene (AC)	6	Vulcan	CH	La/Fla	0.040
												PPG	CH	Oh/La	0.035
2818	Propylene Oxide	.585	8.5	OI-19	12%	6	9	5	80.4	Chlorohydropin (CHLH)	78	BASF			
												Wyandotte	CHLH	Mich	0.107
										via Isobutane (ISB)	22	Dow	CHLH	Tx/Mich/La	0.440
												Oxirane Chem	ISB	Tx	0.250
												Union Carb	CHLH	SC	0.110

TABLE 3 (cont'd.)

CHARACTERIZATION OF PRINCIPAL CHEMICAL'S PRODUCTION

SIC	PRINCIPAL CHEMICAL	ANNUAL PRODUCTION Y-1971 MM.S.T. /YR.	UNIT VALUE (¢/lb)	RANK* (1969)	ANNUAL GROWTH 1961 - 1971	# COS	# Plt.	# St.	% BY TOP 4	MAJOR PROCESS ALTERNATIVE	PROC. %	COMPANY	PROCESS	GEOGRAPHIC LOCATION (STATE)	CAPACITY (MM.S.T. PER YEAR)
2818	Alkyl Leads (TEL/TML)	.326 (1969)	51	OE-11	4%	4	5	3	100	Ethyl Chloride (EC)	100	Dupont	EC	Cal	0.170
												Ethyl Corp.	EC	La/Tx	0.195
												Nalco Chem	EC	Tx	0.033
												PPG Ind	EC	Tx	0.050
2819	Aluminum Oxide	6.64 (1969)	5.7	IO-3	5.5%	15	23	15	>70	Aluminum oxide from bauxite (B)	100	Aluminum Co of Am	B	Ark/Ala/Tx	
												Anaconda	B	Ga	
												Reynolds Metal Co	B	La/Ark/Tx	
												Kaiser Aluminum	B	La	
2919	Aluminum Sulfate	.640 (100% $Al_2(SO_4)_3$)	15	IO-31	2%	25	83	28		From Bauxite	94	Allied	B	29 locations	
												Am Cyan	B	14 locations	
										From Alumina	6	Stauffer	B	10 locations	
2819	Ammonium Chloride	0.027 (1965)	6.55 white 9.45 grey		-0.5%	3	4	4	100	Ammonium sulfate & sodium chloride (AS)	50	Allied	S	NY	0.015
												Dupont	AS	Oh	0.002
										Byproduct of Solvay process (S)	50	Pennalt	AS	Mich	0.013
2819	Boric Acid	0.070	6.9	IO-63	6.3%	3	4	1	100	Acidification of Borax (AB)	~100	Kerr-McGee	AB	Calif	0.042
												Stauffer	AB	Calif	0.034
												US Borax	AB	Calif	0.115

TABLE 3 (cont'd.)

CHARACTERIZATION OF PRINCIPAL CHEMICAL'S PRODUCTION

SIC	PRINCIPAL CHEMICAL	ANNUAL PRODUCTION Y-1971 MM.S.T. /YR.	UNIT VALUE (¢/lb)	RANK* (1969)	ANNUAL GROWTH 1961 - 1971	# COS	# Plt.	# St.	% BY TOP 4	MAJOR PROCESS ALTERNATIVE	PROC. %	COMPANY	PROCESS	GEOGRAPHIC LOCATION (STATE)	CAPACITY (MM.S.T. PER YEAR)
2819	Chromic Acid	0.025	5.15- 5.35	I0-65	5.2%	4	5	4	100	From sodium dichromate(SD)	100	Allied Chem Chemetron Dia. Sham Essex	SD SD SD SD	Md Oh Oh NJ	0.014 0.002 0.007 0.007
2819	Hydrochloric Acid	2.025 (100% HCL)	5.5	I0-24	8%	40	93	27		By-product and Direct Cl_2+H_2	91.1	Allied Dupont		10 plants 4 plants	
										Salt-acid	8.9	Stauffers		7 plants	
2819	Hydroflouric Acid	0.375	20.45	I0-19	11%	9	15	9	82.8	Fluorspan (F)	100	Allied Chem Dupont Al Co of Am Kaiser Alum	F F F F	La/Calif/SC La/Tx Tx La	0.112 0.150 0.045 0.050
2819	Phospheric Acid	6.03	6.95	I0-2	10%	34	55	21	34	Wet (W)	81.3	City Services Freeport Sulfur Co Tx Gulf Sulfur	W W W	Fla La NC	0.6 0.7 0.5
										Dry (D)	18.7	CF Ind Inc	W	Fla	0.65
2819	Phosphorus	0.597	19	I0-3	20%	7	12	6	85	Electric or Blast Furnace Process (EB)	100	Monsanto FMC Corp Stauffer Occ. Pet.	EB EB EB EB	Tenn/Idaho Idaho Tenn/Mont/Fla Tenn	0.240 0.145 0.110 0.070
2819	Sodium[5] Dichromate and Sodium Chromate	0.131	chromate 14.15 dichromate 16	I0-42	1%	5	6	6	>85	Chromate Ore (CO)		Allied Chem Dia. Sham Hercules Malling Kroot Chem PPG Ind	CO CO CO CO CO	Md NJ/Oh NY Md Tx	

TABLE 3 (cont'd.)

CHARACTERIZATION OF PRINCIPAL CHEMICAL'S PRODUCTION

SIC	PRINCIPAL CHEMICAL	ANNUAL PRODUCTION Y-1971 MM.S.T. /YR.	UNIT VALUE (¢/lb)	RANK * (1969)	ANNUAL GROWTH 1961 - 1971	# COS	# Plt.	# St.	% BY TOP 4	MAJOR PROCESS ALTERNATIVE	PROC. %	COMPANY	PROCESS	GEOGRAPHIC LOCATION (STATE)	CAPACITY (MM.S.T. PER YEAR)
2819	Sodium Sulfate	0.264	powdered 8.6 technical 4.5		5%	8	11	8	>90	Sulfur Dioxide with Caustic Soda (S) Byproduct (B)	7.5 92.5	Reichhold Chem Monsanto Kopper Allied	B B B S	Ala Ill Pa Calif/Del	0.145 0.075 0.025 0.015

* Rankings are witnin four categories on the basis of production value. The categories employed are: principal organics (PO), organics intermediates (OI), organic end products (OE), and inorganics (IO).

1. Manufactured in the same process as chlorine.

2. Made by the hydration of ethylene oxide.

3. By 1973 all chlorohydrin plants eliminated.

4. Not necessarily in the top 4.

5. Sodium Chromate is used almost exclusively for the production of sodium dichromate. Thus the productive figures are for sodium dichromate only.

6. Approximate estimate.

7. Only of the synthetic production.

TABLE 3 (cont'd.)

CHARACTERIZATION OF PRINCIPAL CHEMICAL'S PRODUCTION

SIC	PRINCIPAL CHEMICAL	ANNUAL PRODUCTION Y-1971 MM.S.T. /YR.	UNIT VALUE (¢/lb)	RANK * (1969)	ANNUAL GROWTH 1961 - 1971	# COS	# Plt.	# St.	% BY TOP 4	MAJOR PROCESS ALTERNATIVE	PROC. %	COMPANY	PROCESS	GEOGRAPHIC LOCATION (STATE)	CAPACITY (MM.S.T. PER YEAR)
2812	Chlorine	9.34	3.75	I0-5	7%	36	76	26	57	Diaphragm Cell (DC)	72.4	Dow	DC	Tx/Mich/Cal/La	1.58 (1.8)
												PPG	MC	Tx/Oh/SC/La	1.098 (1.2)
	(Sodium Hydroxide)[1]	(9.69)	(3.55 - 7.06)	(I0-6)						Mercury Cell (MC)	24.6	Dia. Sham	MC	Tx/Oh/Ala/Del	0.72 (.75)
2812	Sodium Carbonate	7.14	1.77	I0-15	2%	10	8	8	93	Trona	47.4	FMC	Trona	Wyo	2.25
												Stauffer	Trona	Wyo	0.8
												Allied	Trona	Wyo	0.55
										Solvay	52.6	Allied	Solvay	La/NY	1.8
												BASF	Solvay	Miss	0.8
												Dia. Sham	Solvay	Oh	0.8
2813	Acetylene	.51	9.0	PO-5	2%	11	16	8	67.7	Carbide (C)	40.6	Air Red. Co	C	Ky	0.12
												Monochem Co	PC	La	0.08
										Petroleum & Natural Gas (PC)	59.4	Tenneco	PC	Tx	0.05
												Union Carbide	PC/C	Oh/SC/Tx/La	0.103
2815	Aniline	.17	15	OI-45	10%	6	8	5	88	Nitrobenzene	94	Dupont		Tx/NJ	0.167
												Am Cyan		NJ/SC	0.050
										Others	6	Mobay		SC	0.035
2815	Benzene	3.78	3.0	PO-2	7%	51	79	18	38.0	Coal tax distillation (CT)	10	Union Carbide	P	La/Ill	0.841
										Petroleum (P)	90	Commonwealth Oil	P	P.R.	0.585
												Rep. Steel	CT/P	Ill/Oh/Ala	0.630
												Esso	P	La/Tx	0.73

TABLE 3 (cont'd.)

CHARACTERIZATION OF PRINCIPAL CHEMICAL'S PRODUCTION

SIC	PRINCIPAL CHEMICAL	ANNUAL PRODUCTION Y-1971 MM.S.T. /YR.	UNIT VALUE (¢/lb)	RANK (1969)	* ANNUAL GROWTH 1961 - 1971	# COS	# Plt.	# St.	% BY TOP 4	MAJOR PROCESS ALTERNATIVE	PROC. %	COMPANY	PROCESS	GEOGRAPHIC LOCATION (STATE)	CAPACITY (MM.S.T. PER YEAR)
2815	Benzene Hexachloride	0.003	6.5			1	1	1	100	Benzene and Chlorine(B/C)	100	Occ.Pet. (Hooker Chem Co)	B/C	NY	0.003+
2815	Chlorobenzene	0.243	6.0	OI-84	-2.2%	11	13	10	77	Benzene and Chlorine(B/C)	100	Dow	B/C	Mich	0.175
												Occ.Pet.	B/C	NY/Ky	0.098
												Union Carb.	B/C	Oh	0.060
2815	Phenol	0.870	8	OI-13	8%	21	29	14	69	Cumene Oxidation(C)	64.7	Allied Chem	C	Pa/Ill	0.200+
										Chlorobenzene (CB)	17.0	Dow	C/CB	NJ/Wash/Mich/Tx	0.340
										Benzene Sulfonate (BS)	16.2	Monsanto	C/BS	Tx/Ill	0.270
										Others	2.1	Union Carbide	C/CB	NJ/Oh	0.225
2815	Phthalic Anhydride	.383	8.25	OI-25	7%	13	20	9	50.5	Xylene (X)	59	Allied	X/N	Calif/Oh/P.R.	0.106
										Naphthalene(N)	41	Monsanto	X/N	NJ/Tx	0.105
												Koppers	X/N	Pa/Ill	0.113
												Standard Oil	X	La	0.065
2815	Styrene	2.21	6.6	OI-1	10%	14	17	5	64.5	Ethylbenzene (E)	100	Dow	E	Tx/Mich	1.000
												Monsanto	E	Tx	0.650
												Standard Oil	E	Tx	0.400
												Foster Grant	E	La	0.350
2816	Titanium Dioxide	.652	26-27	IO-8	3%	9	14	11	76.2	Sulfate (S)	49.7	Dupont	C/S	Cal/Del/Tenn	0.202
												Natl Lead Co	C/S	Mo/NJ	0.280
										Chloride (C)	50.3	SMC Corp	C/S	Md	0.078
												Am Cyan Co	S	Ga	0.072

As discussed in the Introduction, changes to the solid wastes generated during production of a particular chemical can arise from any of four, not wholly independent, factors: market growth and decline, process substitution, process modification, and raw material changes. In most instances the change in solid waste can be related to more than one of these factors. For example, the substitution of petroleum for coal tar in the production of "coal tar derivatives" like benzene, as discussed in the Introduction, is a process substitution motivated by a raw material change. Likewise, there are two distinct processes for handling the various grades of titanium dioxide ores (rutile and ilmenite). The so-called chloride process is used for the high grade ore, while the sulfate process is employed for the lower grades. Use of the chloride process has been increasing, reaching 47% of the market in 1972. One of the motivations for use of the chloride process is its avoidance of acid sludge wastes through chlorine recovery and recycling.* Steps to modify the sulfate process so that it includes sulfuric acid reclamation are now underway.

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*Toxic metals content in the chloride waste prevents use in some applications, e.g. waste treatment.

An example of market considerations playing a role in determining the type of solid wastes generated is the decrease in production of alkyl leads due to an environmentally motivated drop in demand. The wastes from alkyl lead production are highly toxic, and are frequently stored, in lieu of an acceptable disposal alternative. Another market-related example is the displacement of sodium carbonate by sodium hydroxide as a source of sodium oxide for some uses, e.g., in the aluminum industry. This decline in demand for the chemical, when combined with its waste disposal problems, has contributed to the shutdown of a number of Solvay plants for sodium carbonate production. Since the Solvay process is one of the largest solid waste producers in terms of quantity, the shift away from this process to use of natural soda-ash deposits (trona) has a significant effect on the volume of solid waste generation from Sector 281.

The increasing importance of the "Oxirane" process as an alternative to the "chlorohydrin" process for propylene oxide manufacture is an example of an ongoing process substitution. At present, the Oxirane process accounts for 27% of the market[35] and its prospects for future growth are buoyed by its ability to avoid the solid waste problems - waste calcium chloride brine - associated with the chlorohydrin process. Dow Chemical Company, which currently has 48% of total industry capacity for propylene oxide, is seeking to integrate their chlorohydrin process with electrolytic chlorine regeneration to get around present waste problems. Since Dow is the nation's largest chlorine producer, it has significant economic incentive for solving the waste problems of the chlorine-based chlorohydrin process. Direct oxidation has already completely displaced the chlorohydrin process for the manufacture of ethylene oxide. Another example of ongoing process substitution is the recent, environmentally motivated move away from the mercury cell electrolysis process to the diaphragm process for chlorine manufacture. This counteracts the gains made by the mercury process since its domestic introduction. It is anticipated that all future growth in electrolysis capacity will be allocated to the diaphragm process.

In considering resource recovery, emphasis was placed on wastes presently causing difficulty or for which recovery processes have been tentatively proposed. Calcium chloride falls in the former category because the extremely large volumes of waste produced by the Solvay process for sodium carbonate appear to be causing the disappearance of that process in the United States. Phosphoric acid belongs to both categories because the present volume of waste is large and also contains significant potential resource value. Several processes have been proposed to abstract hydrofluoric acid from the waste,[36-38] and use as a fertilizer has been suggested.[39] Alumina production (Bayer process) also generates extremely large waste volumes but over several decades no one has yet been successful in abstracting the significant resource value contained therein. Presently, efforts are underway to modify the process itself as a means of avoiding the resource value loss currently suffered. Other instances in which resource recovery can eventually be expected to be introduced (for environmental reasons) have already been mentioned: chlorine recovery from the chlorohydrin process for propylene oxide, and sulfuric acid recovery from the sulfate process for titanium dioxide manufacture. The principal resource potential of the organic wastes seems to be recovery of the Btu content of the waste tars. Alternatively, chlorinated hydrocarbons can be converted to hydrochloric acid, to carbon tetrachloride and perchlorethylene, or to vinyl chloride monomer.

The criterion of difficulty was taken to be that the waste be of exceptionally large and irreducible volume or that the unit cost of disposal significantly exceed the average. Calcium chloride is an example of a large volume waste, being produced in large quantity by both the Solvay process for sodium carbonate and the chlorohydrin process for propylene oxide, as already noted. Likewise, the carbide process for acetylene manufacture produces large quantities of calcium hydroxide waste. In the urban areas where acetylene is typically produced for industrial purposes the disposal of this waste poses something of a problem. The other major large volume wastes produced in the sector are those associated with chlorine, alumina, hydrofluoric acid, titanium dioxide, phosphorus, and phosphoric acid manufacture.

The cases where disposal costs are exceptionally high tend to coincide with particularly undesirable properties, and are discussed in that context. The most important deleterious property is toxicity. In the later stages of this project information became available from EPA's study of hazardous wastes, although by that time most of our determinations had been made.* The largest class of toxic wastes produced in the industrial chemical sector is the chlorinated hydrocarbons. The pesticide benzene hexachloride (trade name lindane) is one example. This is but one of six isomers concurrently produced and the others, having no market, pose a difficult disposal problem. Chlorobenzene is another example. The principal commercial market is for monochlorobenzene, with a lesser market existing for dichlorobenzene. However, the more highly chlorinated products simultaneously produced have little market, and must be discarded. Ethylene dichloride (EDC) is a third example, but here process modification is tending to reduce the problem. In addition to the chlorinated hydrocarbons, there are a number of other producers of toxic wastes in the sector. The alkyl leads have already been mentioned. Mercury loss from electrolytic chlorine production in the mercury cell is a well known problem. Although nearly all mercury loss has been curtailed, concern over this problem appears to have eliminated the mercury cell from participation in future growth in chlorine production capacity. Sodium chromate and dichromate production and chromic acid manufacture release toxic chromates in their solid wastes.

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* Our data was checked, however, against that EPA data applicable to toxic solid wastes generated during industrial chemical manufacture.

In the foregoing we have identified the chemicals selected as representative of Sector 281 in solid waste generation, and have discussed the criteria under which these chemicals were selected. In the next chapter we present the data base developed for the selected chemicals.

V. INDUSTRIAL CHEMICAL SOLID WASTE DATA BASE

In this chapter we present the data base assembled for each of the 33 selected chemicals. In subsequent chapters we draw upon this data base to address the significance of process change; to project the solid waste estimates to 1977 and 1982; to consider the need and potential for resource recovery; and to assess the need for improved waste treatment and disposal. The data base is organized under four headings:

(1) characterization of the production of the principal chemical;

(2) identification of the quantity and chemical composition of the solid waste generated (when more than one production process participates, each is individually assessed);

(3) assembly of information bearing upon the potential for resource recovery; and

(4) characterization of present waste treatment and disposal, and identification of the differential costs associated with improved treatment and disposal.

In the following sections we describe each of these four sets of data.

CHARACTERIZATION OF THE PRINCIPAL CHEMICAL'S PRODUCTION

To characterize production of the principal chemicals data were assembled on the economic value of the annual production, the diversity of processes participating, the geographic location of production, and the rate of change in the quantity produced via each process route.

Economic worth is presented in terms of annual quantity output (million short tons produced in 1971); present unit value (¢/lb.); and rank among chemicals of a particular category, viz. principal organics (PO), organic intermediates (OI), organic end products (OE), and inorganics (IO).[40]

Breadth of process participation was appraised by identifying the major production processes and their percentage of annual production.*

Geographic diversity of manufacture was assessed by determining the number of participating companies, number of plant sites employed, and number of states in which production occurs. This varied widely from one company with one plant producing benzene hexachloride to 51 companies with 79 plants in 18 states producing benzene. The top four companies were identified for each chemical, and the fraction of industry capacity attributable to them was determined. For each company the geographic location of its plants was given (by state) with capacity and production process identified.

Rates of market growth or decline were ascertained for the decade 1961-1971. Rates of change in process participation were estimated, so that changes in the character or waste load could be predicted.** In making these estimates, use was made where possible, of market and process appraisals appearing in the trade journals, such as Chemical Engineering[41], Chemical Engineering Progress[42], Chemical Week[43], Chemical and Engineering News[44], and others. Information gleaned from informal contacts with industry personnel was also employed.

The data gathered to characterize production of the 33 chemicals are given in Table 3.

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* In instances for which the process participation could not be directly determined, an estimate was made based on installed plant capacity for each process.

**The changes in process participation are presented in the chapter on process change.

IDENTIFICATION OF THE SOLID WASTES GENERATED

The solid waste associated with each production process has been identified in terms of its physical form, chemical composition, and annual domestic production. Terms such as acid sludge, brine, or dry powder are employed to describe physical form. Chemical composition is expressed in terms of tons of each identified waste component per ton of product. We are aware that in many instances trace contaminants are present, and that frequently these contaminants exert a disproportionate influence in determining the economics of resource recovery and waste disposal. Where possible we have identified such contaminants, however, they are often related to proprietary aspects of the process and consequently little information is available regarding them. Also, they may vary among the various users of the process, e.g., different catalysts may be employed to accomplish the same end. Our emphasis has been on identifying the primary components of the waste. Annual waste production attributable to a particular process alternative is derived from the fraction of the primary chemical produced by that process.

The data gathered to identify the wastes generated by the 33 chemicals are given in Table 4.

TABLE 4
CHARACTER OF SOLID WASTES

SIC	PRINCIPAL CHEMICAL	PROCESS EMPLOYED	%	SW FORM	Solid Waste Composition	Solid Waste Coefficient (lb/lb product)	Process Solid Waste Production (10^3 S.T.) 1972	Total SW (10^3 S.T.) 1972
2812	Chlorine	diaphragm cell	72.4	brine sludge	NaCl, KCl $CaCO_3$, $Mg(OH)_2$	0.290 0.045	2227.4 339.4	3388.8
	(Sodium Hydroxide)	mercury cell	24.6	brine sludge	NaCl, KCl $CaCO_3$, $Mg(OH)_2$ Na_2SO_4, Hg	0.290 0.025 [100 ppm]	756.8 65.2	
2812	Sodium Carbonate	trona	47.4	impurity sludge	$CaCO_3$ $Mg(OH)_2$	0.098	343.7	5189.9
		solvay	52.6	salt[2]	$CaCl_2$	1.20	4671.0	
				impurity sludge	$CaCO_3$ $Mg(OH)_2$	0.045	175.2	
2813	Acetylene	carbide	40.6	$Ca(OH)_2$ sludge	$Ca(OH)_2$	2.88	589.0	589.0
		petrochemical	59.4	*	*	*	*	*
2815	Aniline	nitrobenzene[1]	94	tars	tars	0.010	1.79	1.91
		other	6	tars	tars	0.010	0.12	
2815	Benzene	coal tar distillation	10	acid and alkali sludge	H_2SO_4/$CaSO_4$ NaOH/NaCl Oils	.030	13.76	13.76
		petroleum	90	*	*	*	*	*

Table 4 (con't)

SIC	PRINCIPAL CHEMICAL	PROCESS EMPLOYED	%	SW FORM	Solid Waste Composition	Solid Waste Coefficient (lb/lb product)	Process Solid Waste Production (10^3 S.T.) 1972	Total SW (10^3 S.T.) 1972
2815	Benzene hexachloride	Benzene/chlorine	100	tar	toxic isomer of BHC	1.0	3.0	3.0
2815	Chlorobenzene	benzene /chlorine	100	tars	chlorinated hydrocarbons O-DCB,p-DCB	0.0266 0.133 [sold as byproduct]	6.97 [34.87]	6.97
2815	Phenol	cumene oxidation	64.7	tars salts	tars Na_2SO_4 Na_2CO_3	0.100 0.081	49.71 50.41	453.28
		chlorobenzene	17.0	tars salts	tars	0.100	16.35 202.78	
		benzene sulfonate	16.2	sludge	Na_2SO_3 $Na_2SO_4{}^2$	1.330 [byproduct] 0.860	[207.27] 134.03	
2815	Phthalic anhydride	xylene	59	tars catalysts	hydrocarbons vanadium	0.205 5×10^{-5}[sold as byproduct]	4.95 [.012]	
		naphthalene	41	tars	hydrocarbons	0.205	3.44	
2815	Styrene	ethylbenzene	100	tars	hydrocarbons	0.027	67.3	67.3
2816	Titanium dioxide	sulfate	49.7	iron, acid sludge	$FeSO_4$ H_2SO_4 TiO_2 inerts	0.860 0.960 0.140 0.120	789.9 880.8 128.5 110.1	

Table 4 (con't)

SIC	PRINCIPAL CHEMICAL	PROCESS EMPLOYED	%	SW FORM	Solid Waste Composition	Solid Waste Coefficient (lb/lb product)	Process Solid Waste Production (10^3 S.T.) 1972	Total SW (10^3 S.T.) 1972
2816	Titanium dioxide (cont)	chloride	50.3	iron sludge	$FeCl_3$	0.611	147.8	2079.5
					TiO_2	0.032	7.74	
					inerts	0.064	5.50	
2816	Zinc oxide	American	60.0	iron sludge	Fe_2O_3, FeO, MgO	4.25	612.0	612.0
		French	28.3	none	none	none	none	
2818	Chloroform	chlorinating methane	95	none	none	none	none	22.94
		acetone and bleaching powder	5	salt and alkali sludge	$CaCL_2$	1.4	11.9	
					$Ca(OH)_2$	0.630	5.35	
					$Ca(CH_3COO)_2$	0.670	5.69	
2818	Ethylene dichloride	ethylene/chlorine	100	tars	chlorinated hydrocarbons	0.009	34.47	34.47
2818	Ethylene oxide	direct oxidation	89.2	none	none	none	none	211.72
	(Ethylene glycol)	chlorohydrin	10.8	salt sludge	$CaCl_2$	1.260	205.52	
					misc. organics	0.038	6.20	
2818	Formic acid	sodium formate	30	sulfate sludge	$Na_2SO_4^2$	1.54	4,38	4.38
		other byproduct	70	none	none	none	none	
2818	Glycerine	allyl chloride	51.8	salts,	$CaCl_2$	0.800	72.52	
					NaCl	0.640	58.02	

Table 4 (con't)

SIC	PRINCIPAL CHEMICAL	PROCESS EMPLOYED	%	SW FORM	Solid Waste Composition	Solid Waste Coefficient (lb/lb product)	Process Solid Waste Production (10^3 S.T.) 1972	Total SW (10^3 S.T.) 1972
2818	Glycerine (con't)	Allyl chloride (cont)	51.8	tars	hydrocarbons	0.078 [maximum]	7.07	139.44
		acrolein	8.4	tars	tars	0.100 [maximum]	1.83	
		propylene oxide[3]	10.5					
		synthetic	29.3	*	*	*	*	
2818	Perchloroethylene	acetylene	6	salts tars	$CaCl_2$ tars	0.670 0.150 [maximum]	3.46	30.76
		chloronation of hydrocarbons	94	tars	tars	0.0326	11.8	
2818	Propylene oxide	chlorohydrin	78	salts tars	$CaCl_2$ tars	0.950 0.038	241.0 9.64	250.64
		isobutane	22	none	none	none	none	
2818	Tetraethyl/Tetramethyl Leads	ethyl chloride		salt sludge	salt lead content of sludge	0.750 0.00075	243 0.243	243.3
2819	Aluminum oxide (alumina)	Bayer	100	sludge	iron Al_2O_3+$Al_2(SO_4)_3$ TiO_2	0.300 0.190 0.060 0.450	2520.0 1596.0 504.0 3780.0	8400.0
2819	Aluminum sulfate	bauxite	93.7	acidic iron sludge	iron inerts H_2SO_4	0.059 0.116 0.005	35.4 69.6 3.0	108.0
		alumina	6.3	none	none	none	none	

Table 4 (con't)

SIC	PRINCIPAL CHEMICAL	PROCESS EMPLOYED	%	SW FORM	Solid Waste Composition	Solid Waste Coefficient (lb/lb product)	Process Solid Waste Production (10^3 S.T.) 1972	Total SW (10^3 S.T.) 1972
2819	Ammonium chloride	ammonium sulfate	50	salts sulfate sludge	NaCl Na_2SO_4	0.157 1.320	1.81 15.21	17.02
		byproduct	50	none	none	none	none	
2819	Boric acid	acidification of borax	100	sulfate sludge	Na_2SO_4 2	0.574	43.4	43.4
2819	Chromic acid	from sodium dichromate	100	sulfate sludge	Na_2SO_4 2	0.710	19.66	19.66
2819	Hydrochloric acid	byproduct and direct H_2Cl_2	91.1	none	none	none	none	
		salt/acid	8.9	sulfate sludge	Na_2SO_4 2	1.98	189.40*	189.40
2819	Hydrofluoric acid	fluorspar	100	sludge	$CaSO_4$ CaF_2 H_2SO_4 silica	3.55 0.06 0.250 0.015	1236.1 20.8 87.1 5.22	1349.2
2819	Phosphoric acid	wet	81.3	gypsum sludge	$CaSO_4$ inerts phosphates	3.36 0.187 0.023	18690. 1040.2 127.9	27158.6
		dry	18.7	slag	$CaSiO_3$ inerts phosphorus	2.3 3.4 0.006	2942.7 4350.1 7.7	
2819	Phosphorus	electric or blast furnace	100	slag	$CaSiO_3$ inerts phosphorus	5.50 2.207 0.006	3954.5 1586.8 7.3	5545.6

Table 4 (con't)

SIC	PRINCIPAL CHEMICAL	PROCESS EMPLOYED	%	SW FORM	Solid Waste Composition	Solid Waste Coefficient (lb/lb product)	Process Solid Waste Production (10^3 S.T.) 1972	Total SW (10^3 S.T.) 1972
2819	Sodium dichromate and Sodium chromate	from chromate ore	100	sludge	Fe_2O_3 inerts Na_2SO_4 chromium	0.250 0.550 0.540 0.017	37.8 83.16 81.6 2.57	205.13
2819	Sodium sulfite	sulfur dioxide with caustic soda	92.5	sludge	Na_2SO_4 [2]	6.25	128.4	128.4
		byproduct	7.5	none	none	none	none	

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[1] Old nitrobenzene process using iron as reducing agent has been completely phased out.

[2] May be sold as a by-product.

[3] Uncertain of waste quantity, believe to be low.

*Outside the scope of 281

APPRAISAL OF THE POTENTIAL FOR RESOURCE RECOVERY

Data gathered to serve as a basis in appraising resource recovery potential included: commercial value of the waste chemical components; present market size for the waste chemicals; identification of resource options; and an approximate index of recovery potential based on market and technology considerations. Resource recovery options are presented in the form of descriptive phases.

The indices of market, technology, and net potential are intended as a partial quantization of the impressions gained by the authors in their process reviews. The index of market potential represents a weighting of the ability of the commercial market to accept that quantity of material and the capability to market the recovered material at a competitive price. Technology potential refers to the present technological capability to carry out the indicated recovery: L means that the technology for recovery is not presently available, M means that the recovery technology is at the pilot plant stage of development, and H means that commercial processes are available. Net potential is an overall average of of the two considerations. In some cases, even though little market demand exists, the net potential is judged medium if other considerations, e.g., environmental, motivate recovery.

The data pertaining to resource recovery from the waste streams of the 33 chemicals are given in Table 5.

TABLE 5

RESOURCE RECOVERY POTENTIAL OF WASTE STREAMS

SIC	PRINCIPAL CHEMICAL	PROCESS EMPLOYED		W FORM	Solid Waste Composition	Process Solid Waste Production (10^3 S.T.) 1972	Commercial Value ($/S.T.)**	Waste Stream Value (MM $)	Commercial Production of Waste Chemical (10^3 S.T.) 1970	Resource Recovery Alternatives	Market Potential	Technology Recovery Potential	Net Potential
2812	Chlorine	diaphragm cell	72.4	brine sludge	NaCl, KCl $CaCO_3$, $Mg(OH)_2$	2227.4 339.4	6.5 44.0	1.47 15.0	43000 [NaCl] 15300 [$CaCO_3$] 87.5 [$Mg(OH)_2$]	evaporation, purification recovery of salt	L	H	L
	(Sodium Hydroxide)	mercury cell	24.6	brine sludge	NaCl,KCl $CaCO_3$, $Mg(OH)_2$ Na_2SO_4, Hg	756.8 65.2	6.5 44.0	4.9 2.9	43000 [NaCl] 15300 [$CaCO_3$] 87.5 [$Mg(OH)_2$]	mercury recovery via oxidation	H	M	M
2812	Sodium Carbonate	trona	47.4	impurity sludge	$CaCO_3$ $Mg(OH)_2$	343.7	44.0	15.1	15300 [$CaCO_3$] 87.5 [$Mg(OH)_2$]	calcium chloride recovery			
		solvay	52.6	salt[2]	$CaCl_2$	4671.0	34.0	15.9	818.5		L	H	M
				impurity sludge	$CaCO_3$ $Mg(OH)_2$	175.2	44.0	7.7	15300 $CaCO_3$ 87.5 $Mg(OH)_2$				
2813	Acetylene	carbide	40.6	$Ca(OH)_2$ sludge	$Ca(OH)_2$	589.0	44.0	25.9	3126 $Ca(OH)_2$	recovery of calcium oxide via calcination	M	H	M
		petrochemical	59.4	*	*								
2815	Aniline	nitrobenzene[1]	94	tars	tars	1.79	4.0	.007	--				
		other	6	tars	tars	0.12	4.0	.002	--				
2815	Benzene	coal tar distillation	10	acid and alkali sludge	$H_2SO_4/CaSO_4$ NaOH/NaCl Oils	8.2 4.1	10 20	0.17	29,300 [H_2SO_4] 9,690 [NaOH]	acid regen., alkalie recovery, recycle catalyst regen.	M	H	H
		petroleum	90	*	*				--		H	H	H

TABLE 5 (Continued)

SIC	PRINCIPAL CHEMICAL	PROCESS EMPLOYED	%	SW FORM	Solid Waste Composition	Process Solid Waste Production (10^3 S.T.) 1972	Commercial Value ($/S.T.)**	Waste Stream Value (MM $)	Commercial Production of Waste Chemical (10^3 S.T.) 1970	Resource Recovery Alternatives	Market Potential	Technology Recovery Potential	Net Potential
2815	Benzene hexachloride	Benzene/chlorine	100	tar	toxic isomer of BHC	3.0	None	None	None	Conversion to HCl	M	M	L
2815	Chlorobenzene	benzene /chlorine	100	tars	chlorinated hydrocarbons	6.97	4.	.027	—	Conversion to HCl	M	H	M
					o-DCB, p-DCB	[34.87]	300.	10.46	61.3	Recover o-DCB & p-DCB	H	H	H
2815	Phenol	cumene oxidation	64.7	tars	tars	49.71	4.	198	—	Recover α-methyl-styrene from tars.	M	H	M
				salts	Na_2CO_3	50.41	31.7	1.59	1360				
		chlorobenzene	17.0	tars	tars	16.35	4.00	.065	—	Recovery sulfate and sulfite.	M	H	H
				salts		202.78	6.5 [NaCl]	1.32	43000 [NaCl]				
		benzene sulfonate	16.2	sludge	Na_2SO_3	[207.27]	90.	18.7	264	Convert chlorinated tars to HCl	M	M	L
					$Na_2SO_4{}^2$	134.03	28	3.75	1360				
2815	Phthalic anhydride	xylene	59	tars	hydrocarbons	4.95	4.	.020	—	Recover vanadium catalyst.	H	H	H
				catalysts	vanadium	[.012]	2240.	.027	5.13				
		naphthalene	41	tars	hydrocarbons	3.44	4.	.014	—				
2815	Styrene	ethylbenzene	100	tars	hydrocarbons	67.3	4.	.269	—	Acid Regeneration	L	M	M
2816	Titanium dioxide	sulfate	49.7	iron, acid	$FeSO_4$	789.9	40	31.6		Convert H_2SO_4 to gypsum.	L	M	M
				sludge	H_2SO_4	860.8	30	26.4	29300				
					TiO_2	128.5	530.	68.1	652				
					inerts	110.1	—	—	—				

TABLE 5 (Continued)

SIC	PRINCIPAL CHEMICAL	PROCESS EMPLOYED	%	SW FORM	Solid Waste Composition	Process Solid Waste Production (10^3 S.T.) 1972	Commercial Value (\$/S.T.)**	Waste Stream Value (MM \$)	Commercial Production of Waste Chemical (10^3 S.T.) 1970	Resource Recovery Alternatives	Market Potential	Technology Recovery Potential	Net Potential
2816	Titanium dioxide (cont)	chloride	50.3	iron sludge	$FeCl_3$ TiO_2 inerts	147.8 7.74 5.50	21.00 530.00 --	3.1 4.1 --	42 652 --	possible regeneration of iron and chlorine from iron chloride	L	M	M
2816	Zinc oxide	American	60.0	iron sludge	Fe_2O_3, FeO, MgO	612.0	11.45 (FeO)	7.0	38600 (F_2O) $Mg(OH)_2$ 87.5	recover Fe_2O_3+FeO	L	M	L
		French	28.3	none	none	none	--	--	--				
2818	Chloroform	chlorinating methane	95	none	none	none	--	--	--	Recover $CaCl_2$ and $Ca(OH)_2$	L	H	M
		acetone and bleaching powder	5	salt and alkali sludge	$CaCL_2$ $Ca(OH)_2$ $Ca(CH_3COO)_2$	11.9 5.35 5.69	34.00 44.00 --	.40 .24 --	818.5 3126 --				
2818	Ethylene dichloride	ethylene/chlorine	100	tars	chlorinated hydrocarbons	34.47	4.00	138	--	HCl from UCAR VCM raw material	M H	H H	H H
2818	Ethylene oxide	direct oxidation	89.2	none	none	none	--	--	--	recovery $CaCl_2$	L	M	M
	(Ethylene glycol)	chlorohydrin	10.8	salt sludge	$CaCl_2$ misc. organics	205.52 6.20	34.00 4.00	6.98 .025	818.5				
2818	Formic acid	sodium formate	30	sulfate sludge	$Na_2SO_4{}^2$	4.38	28.00	.123	1360.0	recover sodium sulfate	M	H	M
		other byproduct	70	none	none	none	--	--	--				
2818	Glycerine	allyl chloride	51.8	salts,	$CaCl_2$ NaCl	72.52 58.02	34.00 6.50	2.46 .377	818.5 43000	recover $CaCl_2$	L	L	M

TABLE 5 (Continued)

SIC	PRINCIPAL CHEMICAL	PROCESS EMPLOYED	%	SW FORM	Solid Waste Composition	Process Solid Waste Production (10^3 S.T.) 1972	Commercial Value ($/S.T.)**	Waste Stream Value (MM $)	Commercial Production of Waste Chemical (10^3 S.T.) 1970	Resource Recovery Alternatives	Market Potential	Technology Recovery Potential	Net Potential
2818	Glycerine (con't)	Allyl chloride (cont)	51.8	tars	hydrocarbon	7.07	4.00	.028	--	--	--	--	--
		acrolein	8.4	tars	tars	1.83	4.00	.007	--	--	--	--	--
		propylene oxide[3]	10.5	--	--	--	--	--	--	--	--	--	--
		synthetic	29.3	*	*	--	--	--	--	--	--	--	--
2818	Perchloroethylene	acetylene	6	salts tars	$CaCl_2$ tars	15.5	34.00	.527	818.5	recover $CaCl_2$	L	H	M
		chloronation of hydrocarbons	94	tars	tars	11.8	4.00	.047	--	--	--	--	--
2818	Propylene oxide	chlorohydrin	78	salts tars	$CaCl_2$ tars	241.0 9.64	34.00 4.00	8.19 .038	818.5 --	recovery of $CaCl_2$	L	H	M
		isobutane	22	none	none	--	--	--	--	--	--	--	--
2818	Tetraethyl/Tetramethyl Leads	ethyl chloride		salt sludge	salt lead content of sludge	243 0.243	6.5 [NaCl] 300.0	1.57 .073	43000 [NaCl] 1380	recovery of lead	H	M	M
2819	Aluminum oxide (alumina)	Bayer	100	sludge	iron $Al_2O_3+Al_2(SO_4)_3$ TiO_2 inerts	2520.0 1596.0 504.0 3780.0	20.00 114.00 530.0 --	50.4 181.9 267.0 --	38600(as iron oxide) 6640(as Al_2O_3) 652	Troth process (recover Fe, TiO_2, Al_2O_3)	H	M	M
2819	Aluminum sulfate	bauxite	93.7	acidic iron sludge	iron inerts H_2SO_4	35.4 69.6 3.0	20.00 -- 30.00	.708 -- .090	38600 (as iron oxide) -- 29300	Troth Process (recovery Fe, TiO_2, Al_2O_3)	H	M	M
		alumina	6.3	none	none	--	--	--	--	--	--	--	--

TABLE 5 (Continued)

SIC	PRINCIPAL CHEMICAL	PROCESS EMPLOYED	%	SW FORM	Solid Waste Composition	Process Solid Waste Production (10^3 S.T.) 1972	Commercial Value ($/S.T.)**	Waste Stream Value (MM $)	Commercial Production of Waste Chemical (10^3 S.T.) 1970	Resource Recovery Alternatives	Market Potential	Technology Recovery Potential	Net Potential
2819	Ammonium chloride	ammonium sulfate	50	salts sulfate sludge	NaCl Na_2SO_4	1.81 15.21	30.80 28.00	.056 .426	43000 1360	sodium sulfate recovery	M	H	M
		byproduct	50	none	none	--	--	--	--				
2819	Boric acid	acidification of borax	100	sulfate sludge	Na_2SO_4 2	43.4	28.00	1.22	1360	sodium sulfate recovery	M	H	M
2819	Chromic acid	from sodium dichromate	100	sulfate sludge	Na_2SO_4 2	19.66	28.00	.550	1360	sodium sulfate recovery	M	H	M
2819	Hydrochloric acid	byproduct and direct H_2Cl_2	91.1	none	none	--	--		--	sodium sulfate recovery	M	H	H
		salt/acid	8.9	sulfate sludge	Na_2SO_4 2	189.40	28.00	5.30	1360				
2819	Hydrofluoric acid	fluorspar	100	sludge	$CaSO_4$ CaF_2 H_2SO_4 silica	1236.1 20.8 87.1 5.22	3.84 51.70 30.00 --	4.75 1.08 2.61 --	15564 2690 29300 --	gypsum recovery	L	H	L
2819	Phosphoric acid	wet	81.3	gypsum sludge	$CaSO_4$ inerts phosphates	18690 1040.2 127.9	3.84 -- --	71.77 -- --	15564 -- --	gypsum recovery	L	H	L
										convert to HF	H	M	M
		dry	18.7	slag	$CaSiO_3$ inerts phosphorus	2942.7 4350.1 7.7	4.50 380.	13.2 2.93	352000 (sand) 597	recovery of $CaSiO_3$ for use as road aggregate	L	H	L
2819	Phosphorus	electric or blast furnace	100	slag	$CaSiO_3$ inerts phosphorus	295[illegible].5 1[illegible]6.8 [illegible].3	4.50 -- 380.	17.8 2.77	352000 (sand) 597	convert to HF	H	M	M

TABLE 5 (Continued)

SIC	PRINCIPAL CHEMICAL	PROCESS EMPLOYED	%	SW FORM	Solid Waste Composition	Process Solid Waste Production (10^3 S.T.) 1972	Commercial Value ($/S.T.)**	Waste Stream Value (MM $)	Commercial Production of Waste Chemical (10^3 S.T.) 1970	Resource Recovery Alternatives	Market Potential	Technology Recovery Potential	Net Potential
2819	Sodium dichromate				Fe_2O_3	37.8	20.00	.756	38600				
	and	from chromate ore	100	sludge	inerts	83.16	--	--	--	sodium sulfate	M	H	M
	Sodium chromate				Na_2SO_4	81.6	28.00	2.28	1360.0				
					chromium	2.57	17.00 [chromate]	.044	41.0 [chromate]				
2819	Sodium sulfite	sulfur dioxide with caustic soda	92.5	sludge	Na_2SO_4 [2]	128.4	28.00	3.58	1360.0	sodium sulfate	M	H	M
	•	byproduct	7.5	none	none	none	--	--	--	--	--	--	--

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[1] Old nitrobenzene process using iron as reducing agent has been completely phased out.

[2] May be sold as a by-product.

[3] Uncertain of waste quantity, believe to be low.

*Outside the scope of 281

** The tar value is $4.00/S.T. which is based upon the heat content (8000 BTU/lb.)

CHARACTERIZATION OF PRESENT AND POTENTIAL FUTURE DISPOSAL PRACTICE

The manner of present treatment and disposal is depicted by identifying waste quantity per plant, potential environmental affects of the solid waste, conventional practice, and resulting costs. The waste quantity per plant was estimated by identifying a typical plant size (for the principal chemical) and normalizing the waste production to this throughout. Conventional treatment and disposal practice is presented in descriptive terms, such as lagooning, slag piling, ocean dumping. The environmental effects of such practice are described in a similar manner. For instance we might note that a given waste increases the turbidity of water body and has a threshold limiting value of X PPM (for toxic wastes). The costs of the various treatment and disposal practices were estimated using values given in the literature. Waste quantity per plant was used as a rough guide to waste treatment throughput. This tends to be an underestimate since each process waste is nearly always combined with other wastes prior to treatment. For this reason, a throughput of four times the typical plant-size process waste was assumed if the treatment or disposal cost seemed sensitive to scale.* Where improvements in disposal practice appear advisable, the differential costs to achieve such improved treatment and disposal were estimated.

The data for solid waste treatment and disposal for the 33 chemicals are given in Table 6.

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* Total costs attributable to that process were based on the actual throughput, of course, with only unit costs being based on large flows.

TABLE 6

SOLID WASTE TREATMENT AND DISPOSAL COSTS

SIC	Principal Chemical	Waste Form	Waste Quantity (10^3 Ton) 1972	Conventional Treatment and Disposal *	Present Costs ($1000)	SW Environmental Effect	Improved Treatment and Disposal	Improved T/D Costs ($1000)
2812	Chlorine (Sodium Hydroxide)	Brine Sludge	3323.6	lagooning, river disposal	3324	Innocuous - non toxic and slightly alkali	Evaporation and recycle of spent brine	9970
		Brine Sludge containing Hg.	65.2	lagooning	195	Hazard related to mercury content	Evaporation, chemical landfill	2608
2812	Sodium Carbonate	Brine Sludge	5189.9	lagooning, river discharge or sold as by product	5190	Affects river salinity	Evaporation and landfill or deep well injection	25950
2813	Acetylene	Calcium Hydroxide Sludge	589.0	lagooning	1178	Minor	Evaporation, landfill	2945
2815	Aniline	Tars	1.91	Incineration, chemical landfilled	15	Minor	Same	15
2815	Benzene	Acid and Alkali Sludge	13.76	Neutralization; discharge into water	138	Minor	Neutralize, landfill	207
2815	Benzene Hexachloride	Halogenated Tars	3.0	Contained piles	6	Minor toxic if containment fails	Incineration with Hcl scrubbing	45
2815	Chlorobenzene	Halogenated Tars	6.97	Burned with HCl scrubbing	104	Minor	Same	104

TABLE 6 (Continued)

SIC	Principal Chemical	Waste Form	Waste Quantity (10^3 Ton) 1972	Conventional Treatment and Disposal *	Present Costs ($1000)	SW Environmental Effect	Improved Treatment and Disposal	Improved TD Costs ($1000)
2815	Phenol	Tars	66.1	Incinerated, chemical landfilled	529	Minor	Same	529
		Salts	252.0	Lagooned, river discharge	252	Affects river salinity	Evaporation and Landfill or deep well injection	1260
		Sulfite & Sulfate	133.6	Landfilled (another 208 lb sold)	400	Minor	Same	400
2815	Phthalic Anhydride	Tars	8.39	Incineration, landfill	67	Minor	Same	67
		Catalyst	.012	Recovered	-----	None	Same	-----
2815	Styrene	Tars	67.3	Incineration, landfill	538	Minor	Same	538
2816	Titanium Dioxide	Iron-acid Sludge	1909.3	Lagooning, ocean dumping	1910	High acidity harmful to ocean biota	Neutralize or regenerate acid; landfill	19100
		Iron-Chloride Sludge	161.0	Lagooning, landfill	483	Minor	Same	644
2816	Zinc Oxide	Iron-oxide Sludge	612.0	Landfill	2448	Minor	Same	2448
2818	Chloroform	Salt Sludge	11.9	Lagooning, river disposal	12	Affects water salinity	Evaporation; landfill	40
		Alkali Sludge	11.0	Neutralization; river disposal	42	Affects water salinity	Evaporation; landfill	60
2818	Ethylene Dichloride	Halogenated Tars	34.47	Landfill or incinerate	172	Minor	Same	172

TABLE 6 (Continued)

SIC	Principal Chemical	Waste Form	Waste Quantity (10^3 TMS) 1972	Conventional Treatment and Disposal *	Present Costs ($1000)	SW Environmental Effect	Improved Treatment and Disposal	Costs ($1000)
2818	Ethylene Oxide	Halogenated Tars	6.2	Incineration, landfill	90	Minor	Process Change	----
		Salts	205.5	Lagooning, sewer disposal	205	Affects river salinity	Process Change	----
2818	Formic Acid	Sulfate Sludge	4.38	Sold as by product or landfilled	7	Minor	Same	7
2818	Glycerine	Salts	130.5	Lagooning, sewer disposal	130	Affects river salinity	Evaporation and landfill or deep well injection	390
		Halogenated Tars	8.9	Incinerated or chemical landfil	133	Minor	Same	133
2818	Perchloro ethylene	$CaCl_2$	15.5	Lagooning, river disposal	16	Affects river salinity	Evaporation and landfill	45
		Halogenated Tars	15.3	Incinerated or chemical landfil	230	Minor	Same	230
2818	Propylene Oxide	$CaCl_2$	241	Lagooning, river disposal	242	Affects salinity	Evaporation and landfill or deep well injection	1000
		Tars	9.64	Incinerated or chemical landfil	145	Minor	Same	145
2818	Alkyl Lead	Lead Sludge	243	Lagooning, treated with ferrous sulfate	2430	Lead runoff - hazardous to aquatic biota	Incineration to convert lead to lead oxide; ion exchange	14580
2819	Aluminum Oxide	Iron Sludge	8400	Lagooning	8400	Generates particulates in the form of fine iron powder	Same, but keep wet to reduce particulates	8400
2819	Aluminum Sulfate	Iron and Sludge	108	Lagooning and neutralization	1080	Generates particulates in the form of fine iron powder	Same, but keep wet to reduce particulates	1080

TABLE 6 (Continued)

SIC	Principal Chemical	Waste Form	Waste Quantity (10^3 T) 1972	Conventional Treatment and Disposal *	Present Costs ($1000)	SW Environmental Effect	Improved Treatment and Disposal	Costs ($1000)
2819	Ammonium Chloride	Salt	1.81	Lagooning, river disposal	2	Affects river salinity	Evaporation and landfill or deep well injection	9
		Sulfate Sludge	15.21	Landfilled or sold as by product	45	Minor	Same	76
2819	Boric Acid	Sulfate Sludge	43.4	Sulfate sold as by product or Landfilled	43	Minor	Same	43
2819	Chromic Acid	Sulfate Sludge	19.66	Sulfate sold as by product or Landfilled	18	Minor	Same	18
2819	Hydrochloric Acid	Sulfate Sludge	189.40	Sulfate sold as by product or Landfilled	380	Minor	Same	380
2819	Hydrofluoric Acid	Gypsum & Acid Sludge	1349.2	Settling pond and treatment to neutralize sulfuric acid	6750	Minor if acid is neutralized	Same	13500
2819	Phosphoric Acid	Gypsum	18690.	Lagooning	18700	Potential for dike failure	Same	18700
		Slag/Inerts	8460.	Landfill	8460	None	Same	8460
		Phosphorus	7.7	Maintain water cover	8	Phosphorus ignites on contact with air	Same	15
2819	Phosphorus	Slag/Inerts	5541.	Landfill	5541	Minor	Same	5541
		Pho phorus	7.3	Maintain water cover	8	Phosphorus ignites on contact with air	Same	14
2819	Sodium Dichromate & Sodium Chromate	Iron Sludge (Chromium)	123.5	Landfilled	600	Chromium toxic to water biota	More stringent landfill requirements	1200
		Sulfate Sludge	81.6	Sold as by product	-----	None	Same	----

TABLE 6 (Continued)

SIC	Principal Chemical	Waste Form	Waste Quantity (10^3 TMS) 1972	Conventional Treatment and Disposal*	Present Costs ($1000)	SW Environmental Effect	Improved Treatment and Disposal	Costs ($1000)
2819	Sodium Sulfite	Sulfate Sludge	128.4	Sodium sulfate sold as by-product or landfilled *	200	Minor	Same	400
281	Selected Chemicals Total		56,515**		70713			141468

* Prior to Stringent

** This includes material sold as byproduct; such material (584×10^3 S.T.) was deleted while making cost estimates.

SUMMARY

The data given in the preceding sections represents the basic data gathered for the selected chemicals. In subsequent chapters this data is amplified in the context of discussing the effects of process change, forecasting solid waste generation in 1977 and 1982, appraising resource recovery possibilities, and evaluating improved waste treatment and disposal options.

VI. MARKET AND PROCESS CHANGE EFFECTS ON SOLID WASTE GENERATION

In this chapter we consider the role played by market and process substitutions in determining the quantity and composition of the industrial chemical waste load. In so doing we address those aspects of waste generation that bear upon the needs and opportunities for resource recovery. Two specific case studies are discussed. In the first, alternative ways of producing sodium sulfate are considered. In addition to being mined in its naturally occurring form, sodium sulfate is generated as a byproduct in production of eight SIC 281 chemicals and during rayon manufacture. The questions addressed in the case study are whether a suitable market can be found for this material, now and in the future, and what effect changes in the ten production processes will have in its generation. The second case study concerns the production of titanium dioxide. Here, the effect process and raw material changes can have on solid waste generation is examined.

In each case study, time trends were constructed from historical data for market and process change. These time trends were formed by extrapolation of production data since 1950*. Both a linear and an exponential fit were attempted using a least-squares approximation.

In the final section of the chapter, five and ten year projections are made for the solid wastes associable with each of the 33 chemicals. The more provocative examples are individually discussed. These projections are important from the standpoint of placing considerations of resource recovery and treatment and disposal in perspective.

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*If the process was commercially employed in 1950. Otherwise, the year of process introduction served as the initial point for the time series.

CASE STUDY OF SODIUM SULFATE

In both case studies the order of presentation is to provide relevant background information, briefly describe the scenarios to be considered, then discuss the scenarios results.

Background

Sodium sulfate is produced by mining the naturally occurring ore and as a byproduct in rayon manufacture and in production of the following chemicals:

(1) hydrogen chloride (from the Mannheim furnace)
(2) phenol (via the benzene sulfonate method)
(3) sodium sulfite (by reaction of SO_2 with sodium carbonate)
(4) sodium chromate
(5) chromic acid
(6) boric acid
(7) ammonium chloride
(8) formic acid

Process substitution is occurring among the production alternatives for hydrogen chloride, phenol, and sodium sulfite. Ammonium chloride is produced by two processes but no change is underway or anticipated. The other chemicals are produced by only one process. The preponderance (73.8%) of commercial sodium sulfate is produced by mining and rayon manufacture, with the other processes playing a minor role. Excess production of sodium sulfate is discarded as solid waste.

Though sodium sulfate is not a toxic substance or rare commodity, it is of interest because of the large volume produced, the diversity of its sources of production, and its being representative of diverse manner in which wastes are produced in the industry. In this case study we focus upon two questions: how will normally occurring process changes effect the volume of sodium sulfate produced? Secondly, how much sodium sulfate can the future commercial market be expected to accomodate, i.e., what is the potential for resource recovery?

The changes occurring among processes producing sodium sulfate as a byproduct are:

(1) HCl from Mannheim furnace -
This is the only process for HCl which generates sodium sulfate, and historically it has been an important source for the sulfate. However, HCl is being increasingly produced as a byproduct of other reactions, and the Mannheim furnace is being phased out. The projected variation of Mannheim participation in HCl manufacture is shown in Table 7.

(2) Phenol via Benzene Sulfonation -
Although there are five processes for producing phenol, only one yields sodium sulfate as a byproduct. In 1970 the sulfonation process accounted for about 16.2% of the phenol produced. The process is phasing out, however, with one of the major producers expected to close down soon. For purposes of projection we assumed that by 1980 no benzene sulfonation plants will be in operation.

(3) Sodium Sulfite from Soda Ash -
Sodium sulfite is produced as a byproduct of resorcinol and of phenol via the benzene sulfonation process. It is also produced synthetically by the reaction:

$$Na_2CO_3 + SO_2 \rightarrow Na_2SO_3 + CO_2$$

A parallel reaction leading to sodium sulfate occurs, such that for every lb. of sulfite produced 6.25 lb. of sulfate is generated. Presently, only 7.5% of commercial sodium sulfite is produced by the synthetic process. However, the

TABLE 7

MANNHEIM FURNACE PARTICIPATION IN HYDROGEN CHLORIDE PRODUCTION

YEAR	HCl PERCENT VIA MANNHEIM FURNACE PRODUCTION
1952	23.7%
1954	19.6
1956	16.4
1958	12.9
1960	9.3
1962	10.0
1964	11.0
1966	9.2
1968	7.1
1970	5.6

benzene sulfonation process, is decreasing in importance as discussed above. Under these circumstances, the amount of sulfite produced by the synthetic route may increase.

Scenarios

The amount of sodium sulfate produced as waste equals the deficit of market demand to the amount produced. That is,

$$W(t) = -D(t) + N(t) + R(t) + \sum_i P_{c_i}(t)\, f_i(t)\, \omega_i$$

where $W(t)$: waste sodium sulfate
$D(t)$: commercial demand for sodium sulfate
$N(t)$: amount of sodium sulfate mined
$R(t)$: sodium sulfate produced as rayon byproduct
$P_{c_i}(t)$: amount of chemical i produced
$f_i(t)$: fraction of chemical i produced by a process* that generates sodium sulfate as waste
and ω_i: amount of sodium sulfate produced per unit of chemical i

All production is expressed on an annual basis and, as indicated, all quantities other than ω_i vary with time. The sum, $\Sigma\, P_{c_i}(t) \cdot f_i(t)\, \omega_i$, is the total amount of sodium sulfate produced as a byproduct in the production of the eight chemicals listed previously. The demand for sodium sulfate, amount produced by mining and as rayon byproduct, and the production rates for the other chemicals, P_{c_i}, were projected forward in time by extension of least squares fits to historical data, as described previously. The variation of the fraction f_i of HCl, phenol, and sodium sulfite produced by processes generating sodium sulfate as byproduct was also projected from time trends.

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*If more than one process for chemical i were to generate sodium sulfate as waste, they would have to be considered separately as their ω's would probably differ. No instances of this occur, however.

Three scenarios were considered. The waste equation was solved for each.

- Scenario 1

  To serve as a baseline, the product mix existing in 1965 is projected into the future with increases in production taken into account. This scenario is intended for purposes of comparison in illustrating the effect process changes have had, and will have, on the generation of sodium sulfate as waste.

- Scenario 2

  It is assumed that increases in sodium sulfate demand are met through processes which do not involve sodium sulfate generation. Synthetic production is held at its 1972 level.

- Scenario 3

  It is assumed that lags in sodium sulfite production caused by phasing out the benzene sulfonation process are met by increasing sulfite production via the synthetic (soda ash) process.

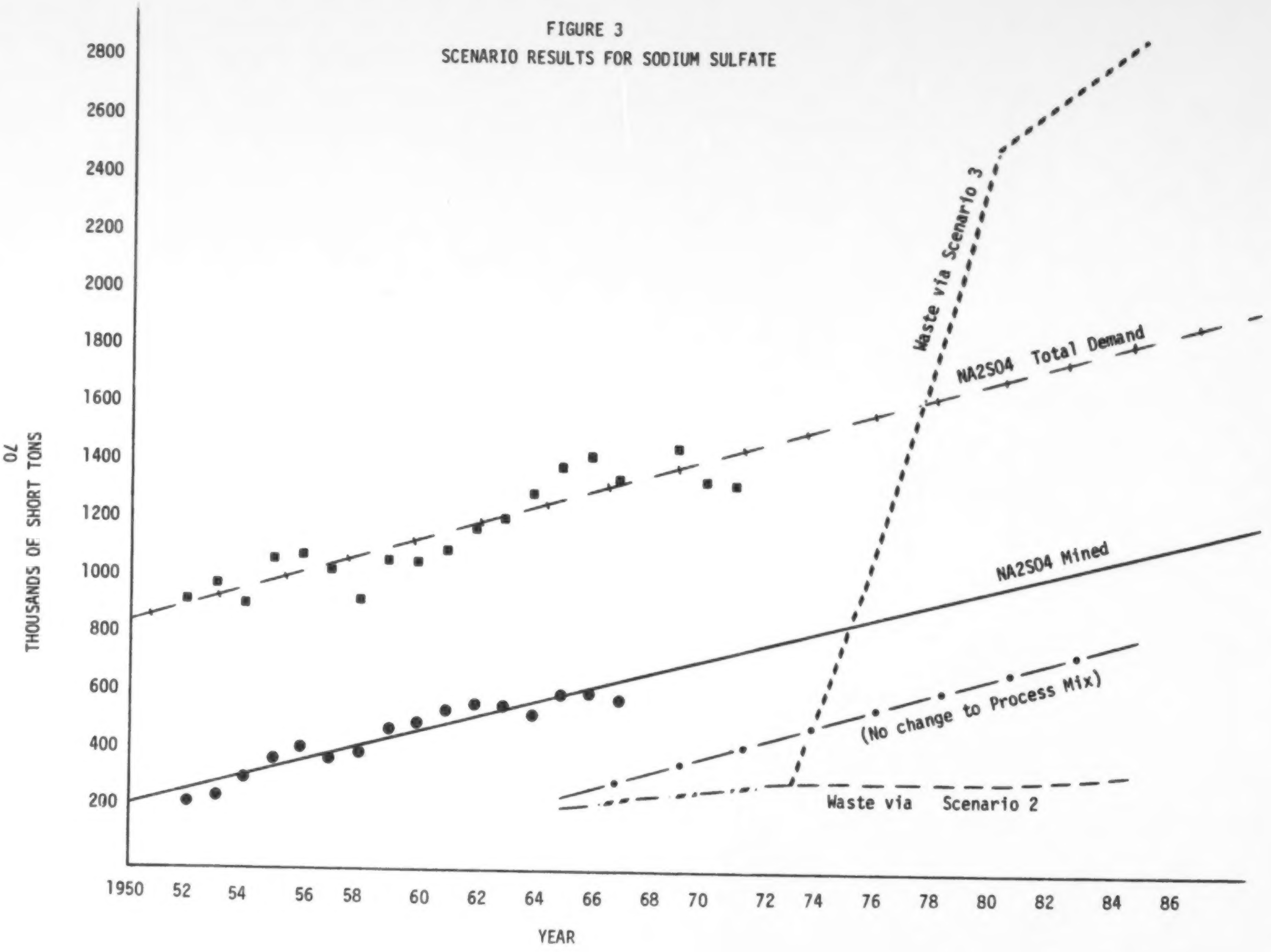
Results

Closest correspondence to historical data for sodium sulfate demand was achieved using a linear least-squares fit. The demand from 1950 to 1971 and its projection to 1984 is shown in Figure 3. Also shown are equivalent data for sodium sulfate mined and that disposed as waste, as determined in the three scenarios. A number of points can be made regarding the scenario results:

(1) Scenario 2 indicates that with synthetic production of sodium sulfite held at its present value ongoing process changes effectively countervail against an increase in solid waste

FIGURE 3

SCENARIO RESULTS FOR SODIUM SULFATE



generation with market growth. A modest increase over the 1965 waste load occurs: 34% by 1972 and 50% by 1982.

(2) In the absence of process changes, the amount of waste sodium sulfate produced in 1972 would be double that produced in 1965, and by 1982 the quantity of waste would increase an additional 67%.

(3) In Scenarios 1 and 2 the amount of sodium sulfate discarded is less than that mined. Thus, if sufficient motivation existed, reduction of sodium sulfate mining could enable market accomodation of the excess sulfate.

(4) In Scenario 3,in which additional sulfite requirements are met through increasing synthesis process participation, sodium sulfate waste generation becomes excessive. Within four years the amount of sodium sulfate discarded as waste becomes equal to the entire market demand. Such a course of events can be modified by employing another alternative for sodium sulfite manufacture or finding ways to increase the sodium sulfate market demand.

The conclusion to be drawn from the results of the three scenarios is that resource recovery does not seem to be the answer for reducing sodium sulfate waste since market demand will not support such a course of action. To penetrate the market, recovered sodium sulfate must be sold at a price competitive with its mined counterpart. Recovery is justified only if:

(1) advantage can be taken of geographic location to minimize transportation costs, or

(2) recovery costs are slight due either to a relatively pure waste stream or a market being found for low purity products, or

(3) the disposal costs are sufficiently high that product recovery and sale at a loss becomes preferrable.

Since sodium sulfate and the materials for manufacturing it abound, there is minimal need for conservation of this resource. Rather, attention should be focused upon proper disposal practice. The benign nature of sodium sulfate presents little difficulty in the achievement of safe disposal through sanitary landfill.

Sodium sulfate is typical of the majority of the wastes produced in the industrial chemical sector. They frequently have slight intrinsic value, and pose little disposal problem. In the next case study we consider a situation in which the wastes do present an awkward disposal problem and the most convenient method of alleviating present difficulties appears to be via resource recovery.

CASE STUDY OF TITANIUM DIOXIDE

Background

A significant quantity of solid waste is generated during titanium dioxide production. A prevalent method for disposal of the wastes has been through discharge into the ocean or a large body of water. American Cyanimid has recently received criticism regarding such disposition of the wastes from its plant in Savannah, Georgia, and the South Carolina legislature has asked EPA to determine whether the water bodies receiving such wastes are being harmed.

- Production Process Alternatives

There are presently two alternatives for producing titanium dioxide: the chloride and the sulfate method. Of the two the chloride process produces solid waste in less volume and of a less hazardous nature.[45] There are two basic steps to the process:

(1) separation of titanium from its ore via chlorination
(2) oxidation of the titanium

For ore of high purity, termed rutile, the chemical reactions are:

(a) TiO_2 (+ impurities) $+ 2C + 2Cl_2 \rightarrow TiCl_4 + 2CO_2 + \ldots$ *
(b) $TiCl_4 + O_2 \rightarrow TiO_2 + 2Cl_2$

In ore of lesser purity, termed ilmenite, the corresponding reactions are:

(a) $TiFeO_3 + C + Cl_2 \rightarrow TiCl_4 + FeCl_3 + CO_2 + CO + FeCl_2 + \ldots$ *
(b) $TiCl_4 + O_2 \rightarrow TiO_2 + 2Cl_2$

In both cases the chlorine is recovered and recycled.

The sulfate process is traditionally employed for the lower grade ores. The reactions that take place are the following:

(a) $TiFeO_3 + 2H_2SO_4 \rightarrow FeSO_4 + TiOSO_4 + 2H_2O$

---

*Coke is used as the source of carbon.

(b) $TiOSO_4 + 2H_2O \rightarrow TiO(OH)_2 + H_2SO_4$

(c) $TiO(OH)_2 \rightarrow TiO_2 + H_2O$

The sulfuric acid produced in the second reaction is quite dilute and is not recovered at present. It is the disposal of acid sludge that has recently been criticised.

- Ores

Three categories of ores are utilized in titanium dioxide production:

rutile	$> 96\%$ TiO_2
high grade ilmenite	$\approx 64\%$ TiO_2; 30% iron oxides
low grade ilmenite	$\approx 44\%$ TiO_2; 45-50% iron oxides

Historically, only rutile has been used in the chloride process, i.e., all ilmenite has been processed using the sulfate method. Recently DuPont opened a plant capable of processing high grade ilmenite using the chloride process; the ilmenite must contain 50% or more TiO_2. This extension of the chloride process offers a significant opportunity for reduction of the solid waste associated with titanium dioxide production.

- Process Modifications

Numerous attempts are being made to modify the present manner of titanium dioxide production. The National Materials Advisory Board recently reviewed the relevant technology.[46] One approach is to recover resource value presently lost in sulfate process wastes. Another is to upgrade low grade ilmenite ore for use in the chloride process.

An example of moves toward recovering resource value from sulfate process wastes is the work of American Cyanimid. In response to regulatory pressure, two alternatives to present handling of their sulfate process wastes are being considered.[47] A process which enables them to recover gypsum following neutralization of the acid sludge appears to be favored. The other process neutralizes the acid, and then discards the waste into the Savannah River. This alternative represents a solution of limited duration in light of the increasing stringency of water pollution regulations.

Attempts to produce a synthetic high grade ore are spurred by a shortage of natural rutile. Such ore offers tremendous processing advantages. One of the more interesting approaches is that of the Benilite Corporation of America. In their process, ilmenite is partially reduced through use of carbonaceous material to convert most of the ferric oxide to ferrous oxide:

(a) $(FeO, Fe_2O_3)\cdot TiO_2 + C \rightarrow FeO\cdot TiO_2 + CO + CO_2$

The reduced ilmenite is leached with 18-20% HCl:

(b) $FeO\cdot TiO_2 + 2HCl \rightarrow FeCl_2 + 2H_2O + TiO_2$

The leached solid is then separated, washed, and calcined. They call the resulting beneficiated ore, "Benilite." The leachate containing ferrous chloride is meanwhile treated to regenerate hydrochloric acid, with iron oxide obtained as byproduct:

(c) $2FeCl_2 + H_2O \rightarrow 2FeO + 2HCl$

The technology for carrying out rutile upgrading in this manner has now been developed. Its implementation is a matter economics, with the cost of rutile being the principal variable.

Scenarios

As described, there are at present two production processes and three types of ores. Rutile and high grade ilmenite are processed by the chloride process and low grade ilmenite is processed by the sulfate process. Therefore, three waste coefficients are needed to determine the solid waste produced during titanium dioxide manufacture:

A_1: the quantity of waste produced by the chloride process employing rutile;

A_2: the quantity of waste produced by the chloride process employing high grade ilmenite;

and A_3: the quantity of waste produced by the sulfate process employing low grade ilmenite.

The values of the waste coefficients per pound of ore are:

$$A_1 \approx 0$$

$$A_2 \approx \begin{array}{l} 0.611\ \mathrm{FeCl_3} \\ 0.032\ \mathrm{TiO_2} \\ \underline{0.064\ \text{inerts}} \\ 0.707\ \text{total} \end{array}$$

$$A_3 \approx \begin{array}{l} 0.96\ \mathrm{H_2SO_4} \\ 0.86\ \mathrm{FeSO_4} \\ 0.14\ \mathrm{TiO_2} \\ \underline{0.12\ \text{inerts}} \\ 2.08\ \text{total} \end{array}$$

The waste equation is then:

$$W(t) = A_1 \cdot R(t) + A_2 \cdot H(t) + A_3 L(t)$$

where $W(t)$: total waste produced

$R(t)$: rutile ore utilized

$H(t)$: high grade ilmenite utilized

and $L(t)$: low grade ilmenite utilized

Three scenarios were considered:

Scenario 1

This scenario was compiled as a baseline in comparing the past and future effects of process change. Rutile participation and the fractional production by the chloride process were maintained at their 1965 levels. A linear fit was employed for titanium dioxide demand.

Scenario 2

Present trends in titanium dioxide production were assumed to continue in the future. In 1965 rutile composed 9.8% of the ore used in TiO_2 production. By 1970 its participation had increased to 14.4%. A linear least squares fit to this trend in rutile participation indicates that by 1977 rutile will compose approximately 20.8% of mined titanium ore. Since the reserves for rutile are diminishing, a further increase in rutile participation seems unlikely. Therefore, beyond 1977 rutile participation was assumed to remain constant at 20.8%.

Scenario 3

In this scenario we made the optimistic assumption that for economic and environmental reasons there will be a rapid introduction of the Benilite process (or an equvalent ilmenite beneficiation technique). Specifically, we assumed that by 1977 50% of the ore being utilized in TiO_2 production will be rutile or Benilite, and that by 1982 the percentage will have risen to 80%. All such high grade, or upgraded, ore is presumed to be processed via the chloride method.* Chloride process participation is thus taken to be 73.5% in 1977 and 90.5% in 1982.

Results

The data employed and the scenario results for solid waste generation are presented in Table 8. These results are plotted Figure 4, together

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*Alternatively, the sulfate method may be improved to an equivalent status (in terms of waste reduction) by that time.

TABLE 8

TITANIUM DIOXIDE SCENARIO DATA AND RESULTS

Scenario 1	1965	1972	1977	1982
Chloride process participation (%)	20.6*	20.6	20.6	20.6
Rutile participation (%)	9.8	9.8	9.8	9.8
Total SW (10^3S.T.)	2232	2606	2891	3177
Scenario 2				
Chloride process participation (%)	20.6*	50.0	67.0	80.0
Rutile participation (%)	9.8	16.4	20.8	20.8
Total SW (10^3S.T.)	2232	2080	1877	1664
Scenario 3				
Chloride process participation (%)	20.6*	50.0	73.5	80.0
Rutile participation (%)	9.8	16.4	50.0	80.0
Total SW (10^3S.T.)	2232	2080	1510	707

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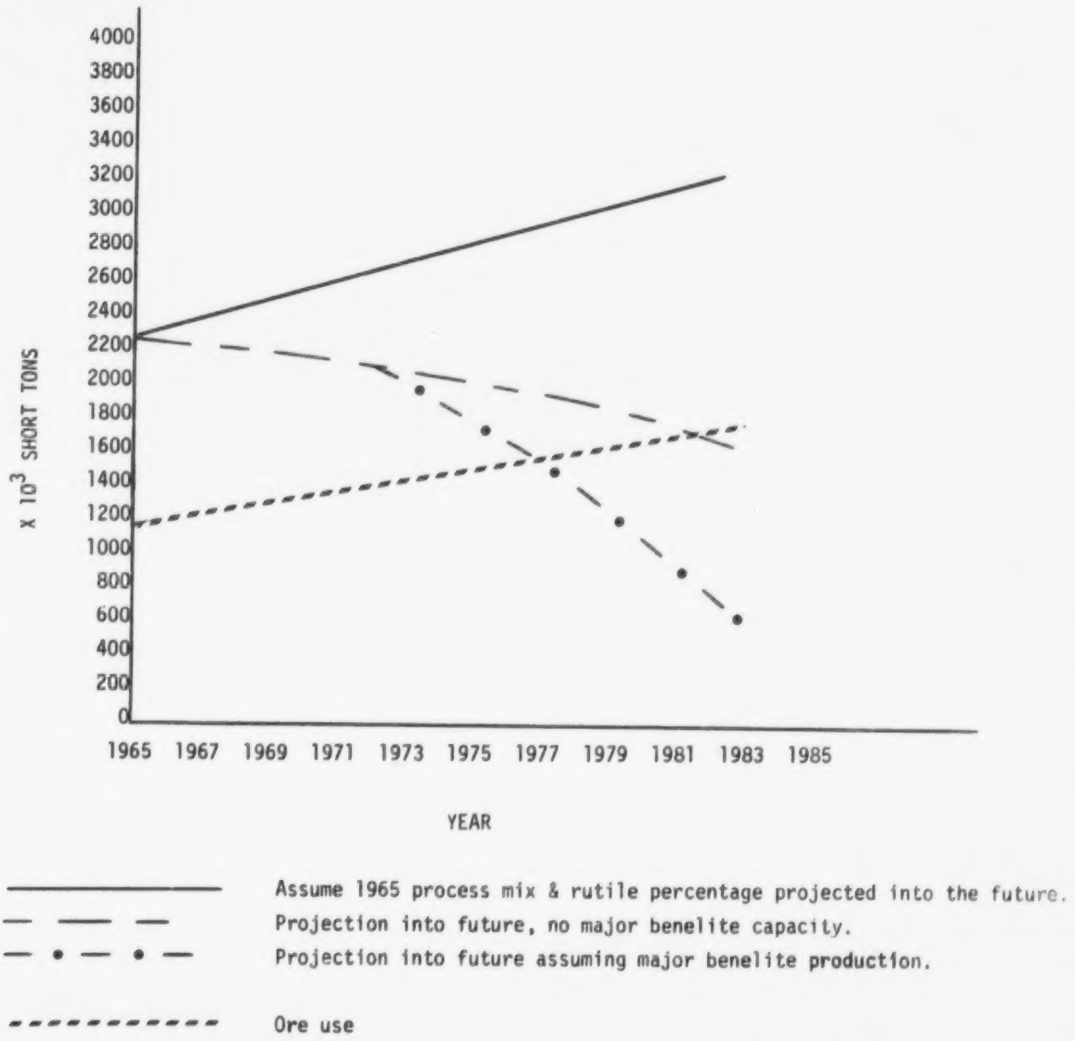
*This percentage was inferred from information presented by the National Materials Advisory Board regarding rutile use. It was assumed that in 1965 only rutile was used in the chloride process.

FIGURE 4

SOLID WASTE GENERATION FROM TiO_2 PRODUCTION



with the time trend in rutile (or equivalent) ore use. Two main points can be made regarding the scenario results:

(1) Clearly, process substitution and changes in raw material usage have a marked impact upon solid waste generation. If present trends continue, the quantity of solid waste in 1982 will have been reduced 25% relative to its 1965 level. This is in marked contrast to the 44% increase that would have occurred in the absence of process change.

(2) The introduction of a process like that employed in Benilite production can make a significant contribution to reduction of the solid waste load. By 1982 the projected use of Benilite would enable a 57% reduction in solid waste load over that anticipated by present trends, and a 78% reduction over that produced if no process substitution or raw material change had occurred. To some extent the solid waste load is merely shifted to the location at which ilmenite is upgraded to Benilite. However, resource recovery can be employed, both through recovery and sale of the iron oxide and through regeneration and recycling of the hydrochloric acid. This enables the avoidance of wastes that would be generated during sulfate processing of such lower grade ores. It should be noted that attempts are also underway to improve the sulfate process in terms of its waste generation properties.

The significance of the trends observed in the titanium dioxide case study is that to a large extent these process substitutions have been encouraged by environmental pressures. The resource value lost in the sulfate process, while significant, was not sufficient by itself to bring about a switch to the chloride process. The environmental advantages of the chloride process have provided an added lure to its utilization, and have added further stimulation to attempts to upgrade ilmenite. The stimulus toward resource recovery has come in this instance from industry's transmutation of environmental regulations into economic decisions.

FIVE- AND TEN-YEAR SOLID WASTE PROJECTIONS

Considerations similar to those presented in the case studies were employed in making five and ten year projections for solid wastes of the 33 selected chemicals. Time trends were constructed for the market growth (or decline) of each chemical and the participation of each process and raw material alternative. Resource recovery was not taken into account. For example, all sodium sulfate byproduct was considered to be a potential solid waste, whereas in our case study we saw that a considerable portion of this material is commercially sold. Likewise, all undesired solids were considered to be solid wastes, even though present disposal practice may be via dilution in air or water streams, e.g., river disposal of salts such as calcium chloride. By 1977 such practices will have been severely curtailed.

Projections were made for the years 1977 and 1982. For comparison, a baseline value was determined for 1977 by assuming no process or raw material changes.

Projection Results

The projections are presented by individual chemical in Table 9, and are summarized from various viewpoints in Table 10. As in the case studies, the effect of process change can be clearly seen. Overall, a 7.3% reduction in the projected 1977 waste load can be attributed to

TABLE 9

PROJECTIONS OF SOLID WASTE GENERATION (DRY WEI

SIC	PRINCIPAL CHEMICAL	1972 Production Figures (10^3 S.T.)	1972 Process Alternatives	%	1972 Solid Waste Projection (10^3 S.T.)	1977 Production** Estimate (10^3 S.T.)	1977 Process Alternatives	%	1977 SW Projection (10^3 S.T.)
2812	Chlorine (Sodium hydroxide)	10608	Dia. cell (DC) Hg cell other	72.4 24.6 3.0	3388.8	15088.	DC Hg cell Other	79.7 17.2 3.0	4846.2
2812	Sodium Carbonate	7400	Trona (T) Solvay (S)	47.4 52.6	5189.9	8600	Trona Solvay	60.5 39.5	4739.1
2812	TOTAL ----------	18008.	----------------	----	8578.7	23688	-------	----	9585.3
2813	Acetylene	511.5	Carbide (C) Petrochem (PC)	40.6 59.4	589.0	511.5	C PC	40.6 59.4	589.0
2813	TOTAL ----------	511.5	----------------	----	589.0	511.5	--------	----	589.0
2815	Aniline	191.0	Nitrobenzene (NB) Other (O)	94 6	1.91	251	NB O	94. 6.	2.51
2815	Benzene	4588.0	Coal tar (CT) Petroleum (P)	10 90	13.76	5778.0	CT P	7.9 92.1	13.69
2815	Benzene Hexachloride	3.0	Benzene/chlorine (BC)	100	3.0	3.0	BC	100	3.0
2815	Chlorobenzene	262.2	Benzene/chlorine (BC)	100	6.97	254.6	BC	100	6.77
2815	Phenol$^+$	962.0	Cumene oxidation (CO) Chlorobenzene (CB) Benzene sulfonate (BS) Other	64.7 17.0 16.2 2.1	453.3	1218.8	CO CB BS O	78.2 13.4 6.3 2.1	438.3
2815	Phthalic Anhydride	399.8	Xylene (X) Naphth. (N)	59 41	8.39	474.1	X N	59 41	9.55
2815	Styrene	2492.3	Ethylbenzene (EB)	100	67.3	3245.7	EB	100	87.63
2815	TOTAL$^+$ ---------	8898.3	----------------	----	554.63	11225.2	--------	----	561.85
2816	Titanium Dioxide	600 (100% TiO_2)	Sulfate (S) Chloride (C)	50 50	2079.5	860.	S C	33 67	1877.1
2816	Zinc Oxide	240	American (A) French (F)	60 40	612.0	280	A F	55 45	654.5
2816	TOTAL ----------	840	----------------	----	2691.5	1140	--------	----	2531.6
2818	Chloroform	170	Chlorination (C) Acetone (A)	95 5	22.94	270	C A	100 0	0
2818	Ethylene dichloride	3830	Ethylene and chlorine (EC)	100	34.47	5340	EC	100	48.0
2818	Ethylene Oxide (ethylene glycol)	1631.2	Direct Oxid. (D.O.) Chlorohydrin (CH)	89.2 10.8	211.72	2033.0	D.O. CH	100 0	0
2818	Formic Acid$^+$	9.47	Sodium Formate (SF) Byproduct and other (BP)	30 70	4.38	9.79	SF BP	30 70	4.5

A

TABLE 9

PROJECTIONS OF SOLID WASTE GENERATION (DRY WEIGHT)

1972 lia Waste rojection 0^3 S.T.)	1977 Production ** Estimate (10^3 S.T.)	1977 Process Alternatives	%	1977 SW Projection (10^3 S.T.)	1977* SW Projection (10^3 S.T.)	1982 Production Estimate (10^3 S.T.)	1982 Process Alternatives	%	1982 SW Projection (10^3 S.T.)	Estimation Procedure
388.8	15088.	DC Hg cell Other	79.7 17.2 3.0	4846.2	4828.6	21460.	DC Hg cell Other	84.8 12.2 3.0	6863.4	#2 - assume no increase in Hg cell capacity
189.9	8600	Trona Solvay	60.5 39.5	4739.1	6031.4	9900.	Trona Solvay	65.7 34.3	4864.9	#4 - closing of solvay plants to continue up to 1977 at a rate equal to that of the last 5 yrs. No further closing or adding capacity after 1977
578.7	23688	-------	----	9585.3	10859.6	31360.	--------	----	11728.3	
589.0	511.5	C PC	40.6 59.4	589.0	589.0	511.0	C PC	40.6 59.4	589.0	Time series is inadequate since recent trend assumes no growth; no process change
589.0	511.5	--------	----	589.0	589.0	511.0	--------	----	589.0	
1.91	251	NB O	94. 6.	2.51	2.51	312.6	NB O	94. 6.	3.13	#4 - no process change expected though the phenol process may become commercial
13.76	5778.0	CT P	7.9 92.1	13.69	17.33	6967.5	CT P	6.6 93.4	13.58	#3 - assume no new coal tar capacity after 1973
3.0	3.0	BC	100	3.0	3.0	3.0	BC	100	3.0	Only one plant produces BHC. Assume that production is maintained at present level
6.97	254.6	BC	100	6.77	6.77	247.2	BC	100	6.58	#3
453.3	1218.8	CO CB BS O	78.2 13.4 6.3 2.1	438.3	573.8	1475.6	CO CB BS O	81.5 11.1 5.3 2.1	480.0	#3 - assume one of the two major benzene sulfonate plants closes. No further chlorobenzene plants
8.39	474.1	X N	59 41	9.95	9.95	548.4	X N	59 41	11.51	#2 - uncertain of process split trend. Assume no change
67.3	3245.7	EB	100	87.63	87.63	3999.1	EB	100	107.9	#3
54.63	11225.2	--------	----	561.85	700.99	13553.4	---------	----	625.7	
79.5	860.	S C	33 67	877.1	2891.4	1000.	S C	20 80	1664.4	#4 see case study #2 for process mix assumptions
12.0	280	A F	55 45	654.5	714.0	325.0	A F	50 50	690.6	#4 - process mix changes at present rate extended into the future
91.5	1140	--------	----	2531.6	3605.4	1325.0	-------	-----	2355.0	
22.94	270	C A	100 0	0	36.3	550	C A	100 0	0	#2 - Acetone bleaching powder process completely eliminated
34.47	5340	EC	100	48.06	48.06	6850.	EC	100	61.65	#3
11.72	2033.0	D.O. CH	100 0	0	263.9	2434.8	D.O. CH	100 0	0	#1 - chlorohydrin method was completely eliminated by 1973
4.38	9.79	SF BP	30 70	4.52	4.52	10.76	SF BP	30 70	4.97	#1 - no knowledge of process trends. Assume for computational purposes no process change

B

TABLE 9 (Cont.)

PROJECTIONS OF SOLID WASTE GENERATION (DRY WEIGHT)

SIC	PRINCIPAL CHEMICAL	1972 Production Figures (10^3 S.T.)	1972 Process Alternatives	%	1972* Solid Waste Projection (10^3 S.T.)	1977 Production** Estimate (10^3 S.T.)	1977 Process Alternatives	%	1977 SW Projection (10^3 S.T.)
2818	Glycerin	175.0	Synthetic Allyl chloride (AC) Propylene Oxide (PO) Acrolein (A) Natural	 51.8 8.4 10.5 29.3	139.44	185.0	Synthetic AC PO A Natural	 63.3 10.3 12.8 13.6	180.11
2818	Perchloro-ethylene	385.4	Acetylene (A) Chlorination of hydrocarbons (CH)	6. 94.	30.76	505.8	A CH	0 100	16.49
2818	Propylene Oxide	325.4	Chlorohydrin (CH) Isobutane (IB)	78 22	250.64	434.4	CH IB	71 29	334.67
2818	TML TEL	326.0	Ethyl Chloride (EC)	100	243.3	326.0	EC	100	243.3
2818	TOTAL --------	6852.5	-----------------	---	937.66	9104.0	------	---	797.2
2819	Alumina	8400.	Acidification(A) Chloride (C)	100 0	8400.	11400.	A C	86.9 13.1	9906.8
2819	Aluminum Sulfate	640	Bauxite (B) Alumina (A)	93.7 6.3	108.0	720	B A	86.9 6.3	121.5
2819	Ammonium Chloride[+]	23.05	Amm. Sulfate (AS) Byproduct (S)	50 50	17.0	22.08	AS S	50 50	16.3
2819	Boric Acid[+]	75.6	Acidification of Borax (A)	100	43.4	82.4	A	100	47.3
2819	Hydrochloric Acid[+]	1074.5	Salt acid (S) By-product and H_2+Cl_2 (B)	8.9 91.1	189.4	1347.3	S B	6.1 93.9	162.7
2819	Hydrofluoric Acid[+]	348.2	Fluorspar (F) From Phosphoric acid plants (P)	100 0	1349.2	429.9	F P	90.5 9.5	1652.5
2819	Phosphoric Acid	6842.	Wet (W) Dry (D)	81.3 18.7	27158.6	11251.	W D	88.7 11.3	42880.9
2819	Phosphorus	719	Dry (D)	100	5545.6	849.5	D	100	6553.5
2819	Sodium Dichromate[+] & Sodium Chromate	151.2	Chromite Ore (CO)	100	205.1	163.3	CO	100	221.6
2819	Chromic Acid[+]	27.7	Sodium Dichromate (SD)	100	19.66	33.6	SD	100	23.86
2819	Sodium Sulfite[+]	274.0	Sulfur Dioxide (S) By-product (B)	7.5 92.5	128.5	320.8	S B	25 75	322.4
2819	TOTAL[+] ----------	18575.	----------------	---	43164.5	26619.8	------	----	61909.4
281	TOTAL ----------	53685.5	-------------------------		56515.0	----- 72289.0	-------------		75974.3

#1 1950 linear fit
#2 1950 exponential fit
#3 1960 linear fit
#4 1960 exponential fit

[+] May sell some of its Na_2SO_4 as a by-product.

*Assuming process mix of 1972.
**Projection from data through 1971.

A

A

TABLE 9 (Cont.)

IONS OF SOLID WASTE GENERATION (DRY WEIGHT)

ste ion** .)	1977 Production Estimate (10^3 S.T.)	1977 Process Alternatives	%	1977 SW Projection (10^3 S.T.)	1977* SW Projection (10^3 S.T.)	1982 Production Estimate (10^3 S.T.)	1982 Process Alternatives	%	1982 SW Projection (10^3 S.T.)	Estimation Procedure
	185.0	Synthetic AC PO A Natural	 63.3 10.3 12.8 13.6	180.11	147.4	210.0	Synthetic AC PO A Natural	 65.9 10.7 13.3 10.1	213.0	#4 - assume present trend for process mix changes extended into the future
	505.8	A CH	0 100	16.49	40.38	626.2	A CH	0 100	20.41	#3 - assume that the acetylene process phased out between 1973 and 1977.
	434.4	CH IB	71 29	334.67	334.67	543.6	CH IB	67 33	359.8	#3 - assume that 50% of all added capacity is the new isobutane process
	326.0	EC	100	243.3	243.3	326.0	EC	100	243.3	It is uncertain whether policy decision will eliminate TML and TEL use in gasoline, thus it was assumed production remains constant
	9104.0	------	---	797.2	1118.5	11551.3	------	---	903.1	
	11400.	A C	86.9 13.1	9906.8	11400	12200	A C	76.3 23.7	9308.0	#4 - assume 50% of new capacity is chloride process
	720	B A	85.9 6.3	121.5	121.5	840	B A	93.7 6.3	141.75	#4 - no process mix change. Lead free aluminum sulfate comes from alumina
	22.08	AS S	50 50	16.3	16.3	21.00	AS S	50 50	15.60	#3
	82.4	A	100	47.3	47.3	89.15	A	100	51.17	#3
	1347.3	S B	6.1 93.9	162.7	237.4	1620.1	S B	4.1 95.9	133.1	#3 - assume present rate of process mix charges are extended into the future
	429.9	F P	90.5 9.5	1652.5	1665.8	511.6	F P	34.1 15.9	1956.0	#3 - assume 50% of added capacity is HF from phosphoric acid plants
	11251.	W D	88.7 11.3	42880.9	44659.9	18501.	W D	93.1 6.9	65869.2	#4 - no more dry process capacity added
	849.5	D	100	6553.5	6553.5	980.1	D	100	7559.5	#3
	163.3	CO	100	221.6	221.6	175.4	CO	100	238.0	#2
	33.6	SD	100	23.86	23.86	40.6	SD	100	28.83	#3
	320.8	S B	25 75	322.4	115.4	367.1	S B	50 50	1147.2	#3
	26619.8	------	----	61909.4	65062.6	35346.2	--------	----	86448.4	
-----	72289.0	-------------		75974.3	61936.1	93646.9	--------	----	102649.5	

duct.

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TABLE 10

SUMMARY DATA FROM PROJECTIONS OF SOLID WASTE GENERATION

	1972	1977*	1977	1982
Inorganics				
2812	8578.7	10859.6	9585.3	11728.3
2813	589.0	589.0	589.0	589.0
2816	2691.5	3605.4	2531.6	2355.0
2819	43164.5	65062.6	61909.4	86448.4
Total	55023.7	80116.6	74615.3	101120.7
Organics				
2815	554.6	701.0	561.8	625.7
2818	973.7	1118.5	797.2	903.1
Total	1528.3	1819.5	1359.0	1528.8
Ore Based**	45272.6	68029.9	63669.9	87218.3
Non-Ore Based	11279.4	13906.2	12304.4	15431.2
All but Phos. Acid	23847.8	30722.7	26539.9	29221.0

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*Waste quantity in 1977 in absence of changes to 1972 process participation.

**Alumina, aluminum sulfate, sodium chromate & dichromate, titanium dioxide, zinc oxide, phosphoric acid, phosphorus, hydrofluoric acid.

process and raw material changes. Among the organics and the non-ore-based materials the reduction is more dramatic, being 25.2% and 11.5% respectively. Even among ore-based materials significant reduction occurs if the masking effect of phosphorus and phosphoric acid waste generation is removed. All other ore-based solid wastes have been reduced 15.5% through process and raw material changes that will have occurred by 1977. The net effect among all 33 chemicals, excluding phosphorus and phosphoric acid, is a 13.6% reduction. In the remainder of this chapter we present the general projection results and individually discuss the more interesting chemicals.

Our projections indicate that after 1977 the growth rate of solid waste production increases. This can be primarily attributed to a diminished influence of presently ongoing process and raw material changes toward alleviation of SW generation. It is to be expected that additional process and raw material utilization changes will be invoked during intervening years, and as a result the projected increased growth rate after 1977 may not occur. We anticipate that changes to the ore-based processes will be of the sort already underway for titanium dioxide. Continuing improvement in the extraction of resource value from the organic raw materials is to be expected. However, in view of the increasing demand for petroleum as an energy source, the shift from coal and inorganic raw materials to petroleum or natural gas feedstocks can be expected to slow, and perhaps be reversed.

Process change, along with product mix changes, will decrease the fractional amount of hazardous waste in the total waste stream as accounted for by the 37 selected chemicals. The recent decline of the mercury cell process for chlorine produce will result in a decrease in the expected mercury waste stream. The limitations placed on some pesticides are reducing the demand for benzene hexachloride and chlorobenzene. Both of these hydrocarbons are toxic.

Significant Process Changes

- Past Changes

Ethylene oxide:

The two commercial methods for production of ethylene oxide have been the chlorohydrin and direct oxidation methods. Direct oxidation of ethylene is the cleaner process, producing essentially no solid waste.[48] The chlorohydrin method, on the other hand, produces a great deal of solid waste. For each pound of ethylene oxide, 1.26 lbs. of calcium chloride and approximately 0.038 lbs. of chlorinated hydrocarbons are produced as undesired byproducts. Since the 1950's use of the chlorohydrin method has been declining, culminating in its total elimination in early 1972. The effect on solid waste is shown in Figure 5.

Perchloroethylene:

Perchloroethylene production has been growing rapidly due to its use in dry cleaning, which accounts for around 75% of its sales. Initially, perchloroethylene was produced from acetylene and chlorine by way of trichloroethylene. Today, however, most is made by chlorination or oxychlorination of other hydrocarbons. The acetylene route produced large quantities of calcium chloride, 0.670 lbs. of $CaCl_2$ per lb. of product. The effect of process change on perchloroethylene's solid waste generation is shown in Figure 6.

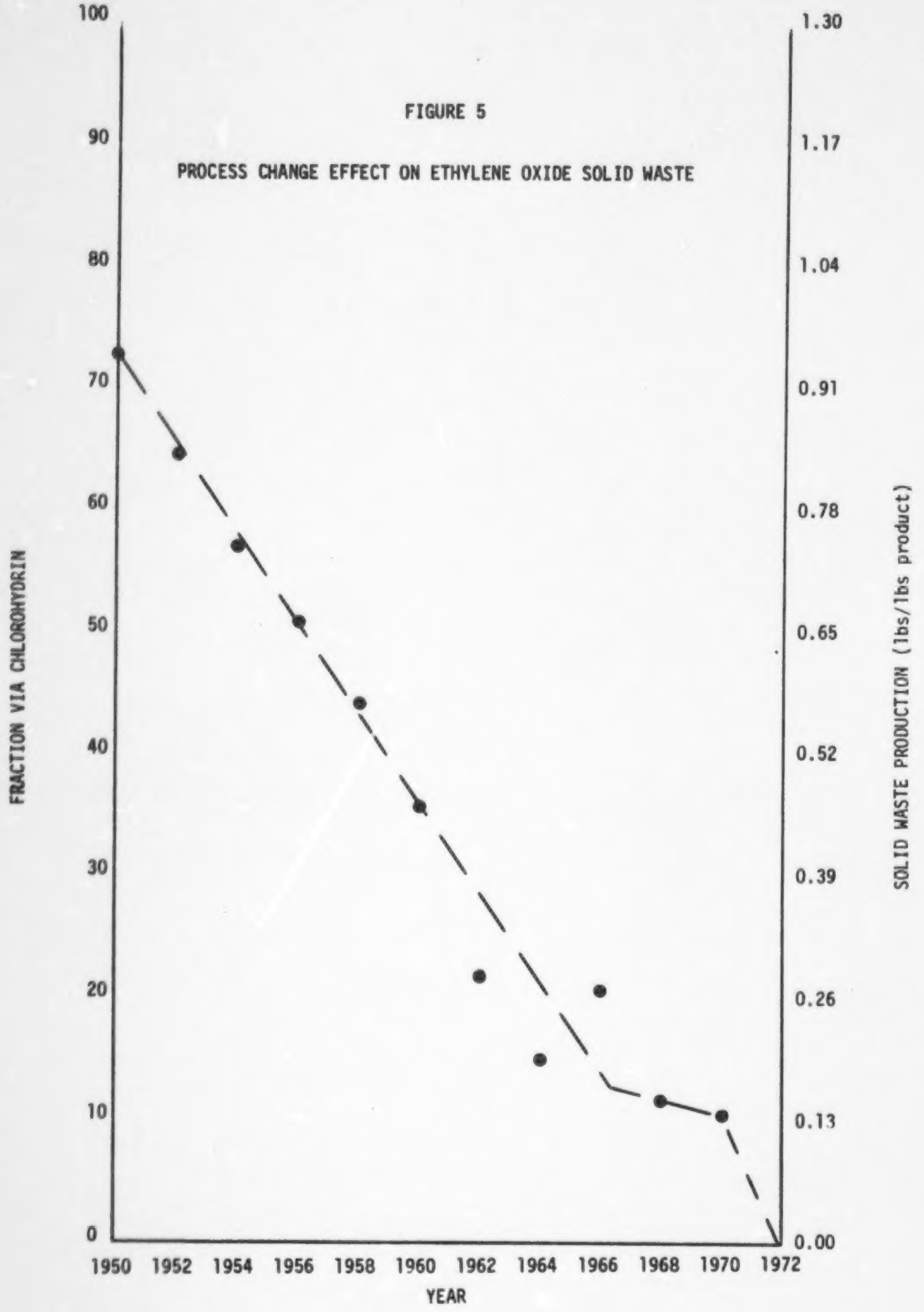
Chloroform:

There are two process for making chloroform: direct chlorination of methane and reaction of acetone with bleaching powder. The reaction sequences are:

1. (a) $CH_4 + Cl_2 \rightarrow CH_3Cl + HCl$
    (b) $CH_3Cl + Cl_2 \rightarrow CH_2Cl_2 + HCl$
    (c) $CH_3Cl_2 + Cl_2 \rightarrow CHCl_3 + HCl$

FIGURE 5

PROCESS CHANGE EFFECT ON ETHYLENE OXIDE SOLID WASTE



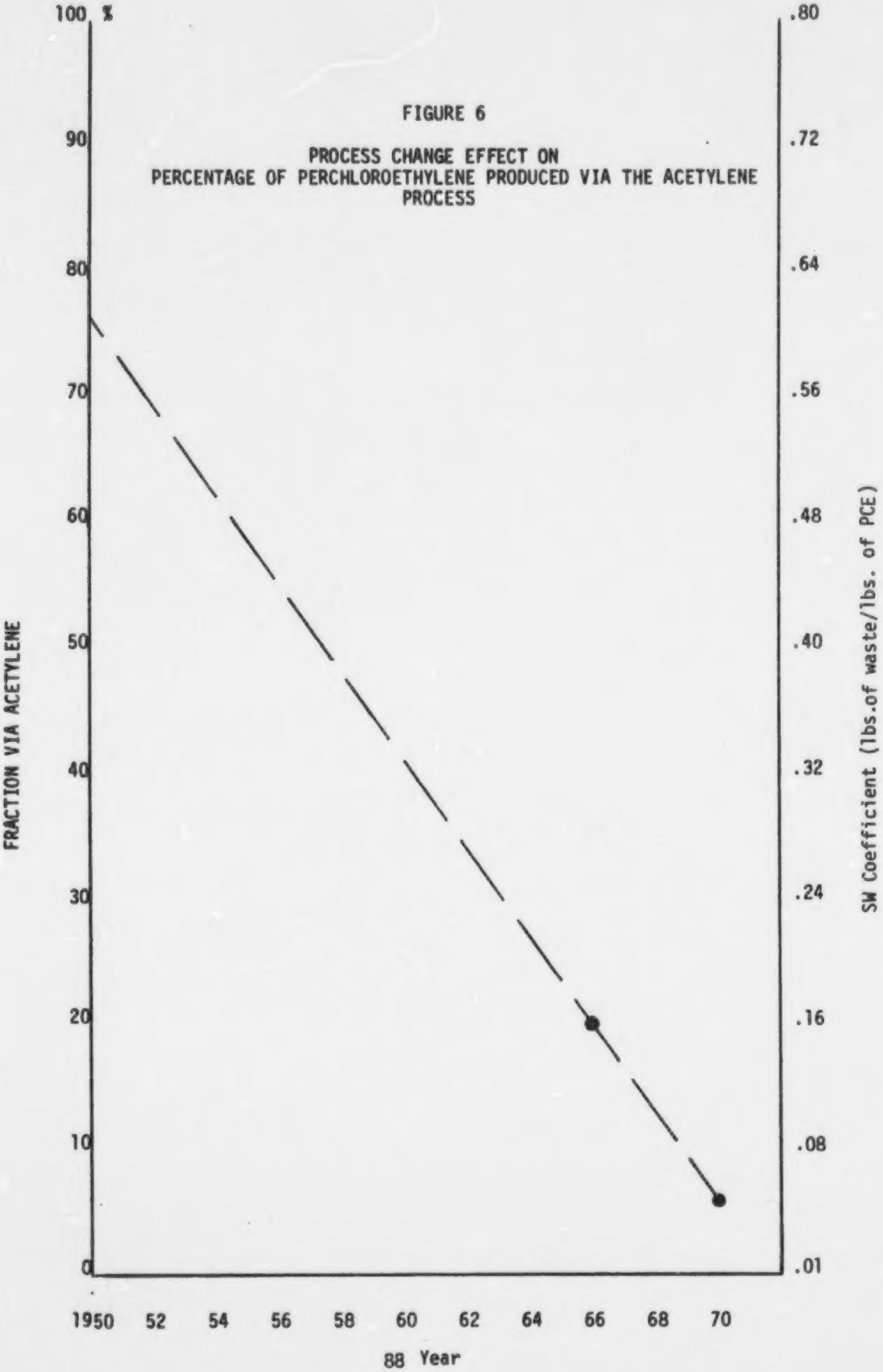


FIGURE 6

PROCESS CHANGE EFFECT ON PERCENTAGE OF PERCHLOROETHYLENE PRODUCED VIA THE ACETYLENE PROCESS

2. $2CH_3COCH_3 + 6CaOCl_2 \cdot H_2O \rightarrow 2CHCl_3 + Ca(CH_3COO)_2 + 2Ca(OH)_2 + 3CaCl_2 + 6H_2O$

The chlorination of methane produces byproduct hydrogen chloride, but essentially no solid waste. In contrast, the acetone and bleaching powder method produces 0.63 lb. calcium hydroxide, 1.4 lb. calcium chloride, and 0.67 lb. calcium acetate per lb. of product. Although the bleaching powder method used to manufacture a significant fraction of the chloroform, it is now nearly extinct. Only one small plant (as of 1968) still made chloroform by the acetone bleaching process.

Hydrochloric Acid:

Hydrochloric acid is primarily produced as a byproduct from chlorinated hydrocarbon manufacture (chloroform being one example) or a principal product from the reaction of sodium chloride and sulfuric acid (Mannheim furnace):

(a) $NaCl + H_2SO_4 \rightarrow NAHSO_4 + HCl$

(b) $NaCl + NaHSO_4 \rightarrow Na_2SO_4 + HCl$

As the reaction sequence indicates, manufacture of HCl via the Mannheim furnace produces byproduct sodium bisulfate and sodium sulfate. As discussed in the sodium sulfate case study, these byproducts end up as waste if the market conditions do not permit their sale. HCl production via the Mannheim process has steadily decreased over the last twenty years. This is shown in Table 7 of the case study.

- Ongoing Changes

Sodium Carbonate (Soda Ash):

This is one of the most striking process changes presently occurring. It can be directly related to difficulties in waste product disposal.

> "By the end of the month PPG's 600,000 tons/day Solvay process plant at Barberton, Ohio, will be added to the growing list of

> shuttered synthetic soda ash units. The high cost of finding ways to dispose of byproduct calcium chloride and competition from lower cost western U.S. natural soda ash generation forced PPG to throw in the towel."[49]

Synthetic production of Na_2CO_3 is by the Solvay process:

(a) $NH_4OH + CO_2 \rightarrow NH_4HCO_3$

(b) $NH_4HCO_3 + NaCL \rightarrow NaH\ CO_3 + NH_4Cl$*

(c) $2NaHCO_3 + \text{Heat} \rightarrow Na_2CO_3 + CO_2 + H_2O$

(d) $2NH_4Cl + Ca(OH)_2 \rightarrow 2NH_3 + CaCl_2 + 2H_2O$

This process produces about 1.2 lb. $CaCl_2$ and .045 lb. other inerts for every lb. of soda ash. Alternative production methods are mining from Trona deposits and extraction from salt lake brine evaporation. Trona ($Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$) contains only about 6% insolubles. Thus the waste problem with Trona is far less severe than with the Solvay process. Natural lake brines are frequently carbonated and contain burkeite ($Na_2CO_3 \cdot 2Na_2SO_4$). The burkeite is processed to form Na_2CO_3 and $Na_2SO_4 \cdot 10H_2O$ (Glauber's salt) plus a number of other byproducts. The Glauber's salt can be sold and disposal of the remaining salts poses no problem since the lake itself is highly saturated. The decline of the synthetic process for producing Na_2CO_3 is illustrated in Figure 7.

Chlorine:

Chlorine is primarily manufactured by electrolysis in either a mercury cell or a diaphragm cell. The diaphragm cell tends to use brine as raw material while the mercury cell uses rock salt, thus the solid wastes from the former are slightly greater. However, the essential difference between the two wastes is that the mercury cell creates highly toxic, mercury containing wastes. The primary problem has been elimi-

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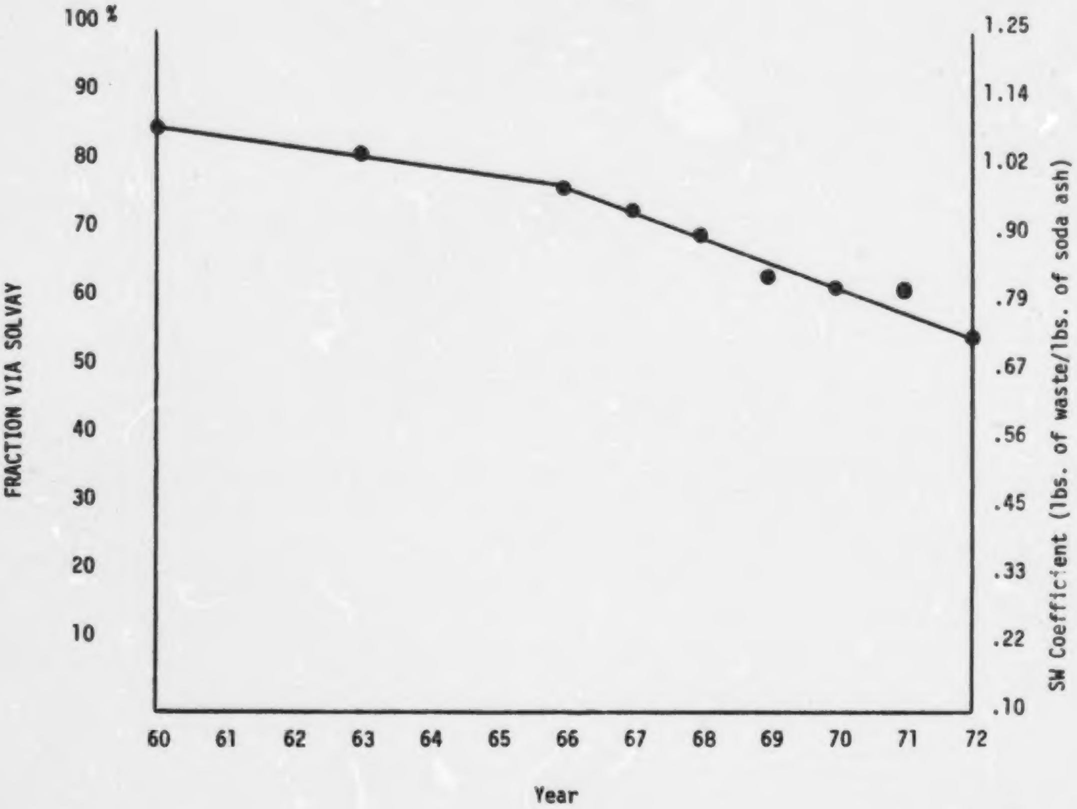
*Some of the ammonium chloride is sold as byproduct.

FIGURE 7

PROCESS CHANGE EFFECT ON
PERCENTAGE OF SODA ASH (NA_2CO_3) PRODUCED VIA
THE SOLVAY PROCESS



nating the mercury wastes to water. This has been essentially accomplished but the cost is high, averaging about 10% of the cost of the original plant. Continuing uncertainty in regulations regarding mercury waste emissions and the high cost of clean up have caused the mercury cell process to fall into disfavor.[50]

> "The Chlorine Institute, which is surveying the U.S. chlorine industry this month, says that in '68, 28.6% of chlorine capacity was mercury cells and 68.1% diaphragm cells. This compares with 24.2% mercury cells and 72.4% diaphragm cells in '72. However, with U.S. chlorine in tight supply, a 22% increase in capacity is now on the drawing boards. And, with the exception of the modernization of a few existing mercury-cell plants, all of the new capacity probably will be diaphragm cells."

Acetylene:

Prior to 1951, all acetylene was derived from calcium carbide. Since then, nine companies have built hydrocarbon acetylene plants and one carbide plant has closed down. No new carbide plants have been constructed in the U.S. within the last three years. By 1966 acetylene produced via the hydrocarbon method had risen to about 60% of total production. In the calcium carbide process large quantities of $Ca(OH)_2$ are produced as a byproduct. About 2.88 lb. $Ca(OH)_2$ (dry weight) is produced for every lb. of acetylene. As waste, the hydroxide poses a disposal problem since many of the acetylene plants are located in populated areas where land value is high. An effort has been made to market the hydroxide.[51] Increased water treatment requirements may boost demand for it.

Propylene Oxide:

Propylene oxide is primarily produced by the chlorohydrin process, as ethylene oxide used to be. However, Oxirane Chemical Co. has installed a plant in Bayport, Texas that produces propylene oxide via direct oxidation of propylene.[52]

> "Halcon-Arco (Oxirane) say that the process is a closed-loop, essentially pollution-free system. To some extent the companies are counting on the anti-pollution movement for an economic booster shot for their process".

The chlorohydrin method produces about 0.950 lb. of $CaCl_2$ for every pound of propylene oxide produced. Our projections assume that 50% of new propylene oxide capacity will employ the Oxirane method.

- Potential Change

Alumina:

Alumina is one of the major solid waste producing chemicals. About one pound of dry weight (2.5-4.0 lbs. wet weight) waste are generated per pound of alumina. At present, nearly all alumina is extracted from its ore (bauxite) via the Bayer process. In this process, bauxite containing 30-55% Al_2O_3 is finely ground and reacted with lime in a caustic soda solution. The sodium aluminate ($Na_2Al_2O_4$) formed is separated, seeded with alumina, and decomposed into aluminum hydroxide. The hydroxide is drawn off and calcined to alumina (Al_2O_3).

The Applied Aluminum Research Corporation (AARC) has developed an alternative process, the "Toth" process. This process begins by chlorinating the bauxite. The aluminum chloride formed is separated and reacted with manganese metal to produce manganese chloride plus aluminum. The manganese chloride is then processed to regenerate manganese metal and chlorine. Both elements are reused. Besides regenerating the chemicals used in the separation process (manganese and chlorine), the Toth process has the potential for recovering resources from the waste.[53]

> "In a subsequent step, fractional condensation separates the metal chlorides. Iron chlorides can be converted to oxides, thereby recovering chlorine. The oxides can be sold. Titanium tetrachloride, a liquid, could be sold for conversion to either metal or oxide. Silicon tetrachloride also could be sold or recycled to limit chlorination of silica".

Work is proceeding on the Toth process. AARC is raising 2 million dollars to design a pilot plant scheduled to begin operation in 1974. Besides having the potential to reduce alumina waste, some of the titanium oxide demand could be supplied as byproduct from the Toth process, thus reducing titanium dioxide waste generation.

VII. RESOURCE RECOVERY NEEDS AND OPPORTUNITIES

At the onset of the project it was found that essentially no organized data base exists for industrial chemical solid wastes. Without such a data base it is impossible to formulate meaningful conclusions regarding the needs and opportunities for resource recovery. Therefore, a primary objective of this project was taken to be the assembly of a base set of solid waste data for industrial chemicals. Emphasis was placed upon the collection and assessment of data pertaining most directly to total sector waste management. That is, attempts were not made to identify a host of innovative resource recovery possibilities, but rather to construct a framework within which the importance of such opportunities can be considered. These were identified in Table 5 and/or are discussed below in the course of considering the overall context of sector resource recovery.

PERSPECTIVE

The assumption has been made in this study that only in the event a scarce resource is being discarded should resource recovery be considered an end in its own right. Otherwise, resource recovery performs a role comparable to other market and process changes wherein they act to reduce the solid waste load. An example of resource recovery as a form of waste reduction is the recovery of gypsum from titanium dioxide (sulfate process) wastes, as discussed previously. Regulatory imposition of waste disposal controls has sufficed, in this case, to set in motion economic forces that are encouraging recovery of (low value) resources.

As stated in the Introduction, emphasis was not placed upon the identification of valuable trace materials present among the solid wastes, e.g., spent catalysts. While such a catalog of valuable materials would be useful, it was necessary first to delineate the bulk composition of the waste. Four points should be made in this regard:

(1) trace components frequently vary from company to company, with their exact composition often a closely held secret; therefore, it is difficult to draw general conclusions regarding their presence;

(2) we found the industry adept at taking advantage of specific, valuable commodities present in the waste stream;

(3) a number of computerized indexing schemes are being developed[54-55] to correlate generation and use of intrinsically valuable commodities; and finally,

(4) trace materials frequently pose waste disposal problems and as such their identification to pollution regulatory bodies is necessary, but was beyond the scope of this study.

The primary resource content of the wastes associated with the 33 selected chemicals is listed in Table 11. As can be seen in this table, the waste chemicals are mainly very low value materials. However, their total commercial value, if a market were found for them, is 11.9% of the $7.20 billion production value of the 33 principal chemicals.* Considering them individually:

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*The 854 million dollars contained in the solid wastes of the 33 chemicals can be compared with an estimate of 2 billion dollars for wastes of all types from the entire sector.[56]

TABLE 11

RESOURCE VALUE AND COMPOSITION OF SOLID WASTE FROM THE 33 SELECTED CHEMICALS

I RESOURCES IN WASTE

Chemical	Waste and Dry Weight (10^3 S.T.)	Commercial Production (10^3 S. T.)	Unit Commercial Value ($/S.T.)
Calcium Sulfate (gypsum)	19926	15564	3.84
Salts and other inerts	16889	43000 (NaCl)	6.50 (NaCl)
Slag (CaS_1O_3)	6897	355000 (S_1O_2)	2.25
Calcium Chloride	5224	818	34.00
Iron Compounds	4143	38600 (FeO and Fe_2O_3)	11.45
Sulfuric Acid in Sludges	985	29300	30.00
Sodium Sulfate	640	1360	28.00
Titanium Dioxide	640	652	530.00
Calcium Hydroxide	594	3126	44.00
Fluorspar	164	252	51.75
Tars (non-halogenated)	153	-	4.00 *
Tars (halogenated)	94	-	4.00 *
TOTAL PRODUCTION	+ 56515		

II NOW SOLD AS BY-PRODUCTS **

Na_2SO_4	345	1360	28.00
$CaCl_2$	139	818.5	34.00
$CaSO_4$	100	15564	3.84
BYPRODUCT SALES	- 584		
TOTAL SOLID WASTE	+55931		

* Heat content value

**Also small quantities of CaS_1O_3 and $Ca(OH)_2$

Titanium Dioxide

The titanium dioxide content of the waste streams practically equals the total titanium dioxide market demand (1970). As indicated in Table 5, most of the TiO_2 is contained in alumina waste. Efforts have been made for over 50 years to extract this resource. So far they have been unsuccessful. As indicated in the discussion of process change, the Troth process for producing alumina may enable titanium dioxide recovery.

Calcium Chloride

Generation of calcium chloride exceeds its market demand, so that even if processors wish to sell their byproduct calcium chloride at a low price, the present market cannot accomodate the available quantity. As a result, processes generating calcium chloride are having economic difficulties, e.g., the Solvay process for soda ash and the chlorohydrin process for ethylene oxide.

Acetylene

As indicated in the previous chapter, generation of large quantities of waste calcium hydroxide within an urban setting has caused disposal difficulties for acetylene manufacturers. Use of calcium hydroxide in water treatment may increase demand for it, enabling its sale as a byproduct.

Sodium Sulfate

Refer to the first case study on process change effects on solid waste generation.

Sulfuric Acid

Environmental considerations are increasing interest in regenerating sulfuric acid from waste sludges. The sulfate process for titanium dioxide, which produces the majority of the acid sludge in Table 11, is a specific example of this.

Hydrofluoric Acid

Discussed in the phosphorus and phosphoric acid case study (next section).

Iron Compounds

There has been little effort to regenerate iron from waste streams. Process changes occurring in titanium dioxide and alumina may generate iron oxide as a byproduct. This is primarily done to recapture the chlorine.

Calcium Sulfate

Discussed in the phosphorus and phosphoric acid case study (next section).

Tars

Tars can be burned on site, and thus do not pose a solid waste disposal problem. In addition, their heat of combustion can be recovered, and so they have (at least potential) resource value. Halogenated tars are less likely to be incinerated because they produce HCl, which is highly corrosive.

Hazardous Substances

Resource recovery of hazardous materials is highly dependent upon economics. For example, the lead content in the waste from production of TEL, TML is recovered to make the process more economic, however, recovery of arsenic from copper smelting is not economic since there is a glut of arsenic on the market.

In the remainder of this chapter we consider the possibilities for resource recovery from the voluminous wastes generated during phosphorus and phosphoric acid production, and discuss general approaches being taken toward facilitation of resource recovery.

CASE STUDY OF PHOSPHORUS ACID

Background

In 1972 phosphorus and phosphoric acid production generated about 57% of the total (dry weight) solid waste from the 33 selected chemicals. Because of the preponderance of this waste, it is important to ascertain whether either resource recovery or process change can be expected to significantly reduce the volume of waste or the associated environmental problems.

All phosphoric acid produced in the world today is derived from phosphate rock ($Ca_{10}(PO_4)_6F_2$). There are two processes for converting the rock into phosphoric acid: a wet process involving its acidulation; and a two step thermal reduction-oxidation process that first produces phosphorus, then phosphoric pentoxide (P_2O_5), and finally phosphoric acid.

The wet process involves the following chemical reactions:

$$3Ca_{10}(PO_4)_6F_2 + 30H_2SO_4 + SiO_2 + 58H_2O \rightarrow$$
$$30CaSO_4 \cdot 2H_2O + 18H_3PO_4 + H_2SiF_6$$

Impurities such as aluminum, silicon, iron and sulfur add to the volume of solid waste from this process. The resulting solid waste stream can be dissaggregated into the following components (per lb. of 100% H_3PO_4) :

3.360 #	$CaSO_4$
0.034 #	CaF_2 (from abatement of H_2SiF_6)
0.091 #	PO_4
0.085 #	Silicon, Al, Fe
3.470 #	Total

In the dry process phosphate rock is smelted with coke and silica in an electric (or blast) furnace to produce elemental phosphorus. Most of the phosphorus is converted to high purity phosphoric acid by oxidation to P_2O_5 vapor, which is then absorbed in water. A simplified version of the reaction is:

(a) $Ca_3(PO_4)_2 + 5C + 3SiO_2 \rightarrow 2P_4 + 3CaSiO_3 + 5CO$

(b) $2P + 5CO + 5O_2 \rightarrow P_2O_5 + 5CO_2$

The dry process generates more waste per unit product (100% H_3PO_4) than the wet process:

2.30 # $CaSiO_3$
3.43 # inerts (FeO, SiO_2...)
0.006 # P_4
5.637 # Total

The greater solid waste load from the dry process is partially the result of its using a lower grade ore. Also, the higher grade ore used in the wet process is further upgraded through beneficiation to relatively pure ($Ca_{10}(PO_4)_6F_2$) fluorapatite. The waste associated with the beneficiation process is not included within the chemical industry, but of course must be environmentally accommodated.

Process change has been occurring in the phosphorus/phosphoric acid industry over the last thirty years.

Year	% thermal (dry)/total
1940	45%
1945	50%
1950	49.6%
1955	41%
1960	36.5%
1965	26.2%
1970	- 20%

The wet process achieved its predominance in the market by exploiting economies of scale, particularly in fertilizer production. As a result of this process substitution, the unit volume of waste produced in the chemical industry has been reduced. As noted above, this is primarily a change in waste bookeeping.

Resource Recovery

Since process change is not acting to reduce the solid waste load, other alternatives should be examined. Resource recovery would be the preferred method. The two largest wastes are gypsum ($CaSO_4 \cdot 2H_2O$) and slag ($CaSiO_3$). In 1972 about 18.69 x 10^6 S. T. of $CaSO_4 \cdot 2H_2O$ and 6.897 x 10^6 S. T. of $CaSiO_3$ were generated from phosphoric acid and phosphorus production alone. Unfortunately, both gypsum and slag are plentiful in nature and as a result their sales price is low.[57]

> "Other than for road building and fill, it [slag] is generally a worthless waste product, and can not be counted on to return a credit to the phosphorus operation. Places like Florida, where natural aggregate is scarce, may be an exception, and a limited market for both regular and expanded slag exists"

Gypsum, the other major byproduct, is usually placed in sanitary landfill or simply piled up. In 1970 9.436 x 10^6 short tons of gypsum were mined and another 6.128 x 10^6 S.T. were imported. Although this market potential exists, the sales price of $3.72 per ton is too low for phosphoric acid manufacturers to sell except in local markets. However, this is not true in Japan where a shortage of natural gypsum leads to a higher market price.

> "These Japanese companies offer processes based on the initial formation of calcium sulfate in the semihydrate form ($CaSO_4 \cdot 1/2\ H_2O$) which is ultimately hydrated to produce an especially high quality gypsum. Simultaneously, a high P_2O_5 recovery, from 97-98.5%, is achieved. The byproduct gypsum thus produced may be used in wall board manufacture, and reportedly sets the government standard for the Japanese plasterboard industry. This type of process was originally developed in Japan because of the lack of high quality natural gypsum resources in that country, and also to effect some economic recovery of the sulfur required for phosphoric acid manufacture."[58]

Even if the byproduct gypsum could displace the naturally mined gypsum there would still be a significant solid waste load since byproduct production of gypsum from all chemical processes [19.92 x 10^6 S.T.] exceeds the total market demand [15.5 x 10^6 S.T.]. Furthermore, phosphoric acid demand is growing at a rapid rate while gypsum demand has remained steady for the last 6 years. Thus, the gap between byproduct production and demand is going to widen. Also, known reserves of natural gypsum contain about 20 billion tons or approximately 2000 years supply at current usage rates.[59] Consequently, the recovery of gypsum from U.S. phosphoric acid plants is not going to be motivated by resource conservation considerations.

Production of hydrofluoric acid as a byproduct of phosphorus and phosphoric acid manufacture is presently being investigated as a resource recovery possibility.[60] Interest has been stimulated by a projected shortage of hydrofluoric acid. It is produced by reaction of high grade fluorspar (CaF_2) with sulfuric acid:

$$CaF_2 + H_2SO_4 \rightarrow CaSO_4 + H_2F_2$$

Demand for hydrofluoric acid has grown at a rapid rate, 11% annually for the decade of the 1960's, and this growth is expected to continue indefinitely. The accelerating demand is depleting domestic fluorspar supplies. (According to the Bureau of Mines, all fluorspar will have been utilized by 1993-1995.) Although phosphate rock contains only 3% fluorine, rock reserves are so large that development of an economic process for recovering its fluorine content will increase U.S. fluorine reserves fifty-fold.[61]

Two processes have been examined for recovering hydrofluoric acid from phosphoric acid and phosphorus wastes. Silicon fluoride (SiF_4) is produced in both processes. Once formed, the SiF_4 vapors are captured in water to produce fluorsilicic acid.

$$3SiF_4 + 2H_2O \rightarrow 2H_2SiF_6 + SiO_2$$

In one of the methods, the fluorsilicic acid is reacted with ammonia to form ammonia fluoride.

$$H_2SiF_6 + 6NH_3 + 2H_2O \rightarrow 6NH_4F + SiO_2\downarrow$$

The ammonia fluoride is heated with calcium hydroxide to produce synthetic fluorspar (CaF_2).

$$6NH_4F + 3Ca(OH)_2 + \cancel{3H_2O} \rightarrow 3CaF_2 + 9H_2O + 6NH_3\uparrow$$

which then is treated in the conventional manner to generate hydrofluoric acid. The second method involves a one step conversion from fluosilicic acid to calcium fluoride, but according to a Bureau of Mines study the process is more difficult to perform.[62]

The reduction in solid waste volume which accompanies the recovery of fluorine is slight, and, the synthetic fluorspar produces large quantities of gypsum when converted to hydroflouric acid. Thus, this process serves as an example of a case in which market conditions are acting to bring about resource recovery for its own sake.

GENERAL APPROACH

In the foregoing discussion we have considered the overall perspective for resource recovery in the industrial chemical sector and addressed a prominent candidate for such recovery. In general terms, our assessment indicates that resource recovery should be considered as one facet of solid waste management, not necessarily preferable to proper waste disposal. Economic considerations appear to act as a sufficient screening device for insuring that a valuable resource is not discarded. There are instances in which resource recovery should and will be employed for its own sake, however, and in the following sections we consider two, not independent, devices for assisting such recovery.

"Junkie" Dealers

Junkie dealers are those commercial enterprises which serve as middle men in waste recovery - receiving waste from its originator, recovering the desired resource value, and selling the recovered material, perhaps back to the original source. There are many such dealers in the United

States, but their numbers are thinning*, with competitive forces favoring the larger enterprises such as International Mills Service and Heckett Engineering. At a recent AIChE meeting, an excellent review was presented of the opportunities and pitfalls associated with operation as a junkie dealer.[63] The primary difficulty lies in insuring continuity in both the raw material, i.e., waste supply and the market demand for the recovered resource. Process or raw material changes, such as those we have discussed, may act to curtail waste generation by the originating processor. Faced with such uncertainty in supply, the dealer must nevertheless be able to provide assurances of product delivery to his customers. Clearly, there is an advantage where the waste being regenerated can be returned to the original processor. And, of course, some processes or participating materials, such as catalysts, are less subject to change.

In spite of the difficulties, there is a function to be provided by such junkie dealers. The larger companies are frequently not geared to either processing or selling the recovered resource, which is usually produced in much smaller quantity than the primary product. The higher overhead usually associated with a large company hinders effective competition against contenders to the recovered material, the sales staff is not geared to low quantity sales, and there are frequently alternative investment opportunities which afford a higher return. Thus, it is frequently in the interest of the large company to cooperate with the junkie dealer, however, not to the extent that it interferes with the main process or its modification.

The question arises as to whether it is appropriate for the government to provide assistance to junkie dealers. In line with our previously stated conclusion that economic forces appear sufficient to prevent scarce resource loss, our answer tends to be in the negative. The issues to be addressed in consideration of the junkie industry are those appropriate to any small business, and are not specific to industrial chemical manufacture. As such, it would seem that steps to provide a healthful climate for small business while not unduely interferring with the normal course of business would be useful. Such steps include support of research on fundamental recovery operations, such as sludge reduction and treatment, and development of enhanced data handling schemes. The government is already acting in both these areas. The latter is discussed next.

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*We were unable to obtain a meaningful estimate of the number of junkie dealers. Most are small, having a $50,000 annual profit or so. Tonnage is highly variable.

Improvements in the Data Base

This report represents one step toward improvement of available information on industrial chemical wastes. There are a number of complementary efforts underway. The work of A. D. Little to develop a classification scheme for industrial solid wastes is one example.[64] The 16 month ADL study was sponsored by the same EPA project office-The Solid and Hazardous Waste Research Laboratory, National Environmental Research Center, Cincinnati, Ohio-and was performed in parallel with the present study. The classification scheme attempts to provide a waste designation containing sufficient information to enable identification of resource recovery opportunities. Data of the following type are included:

(1) plant data - SIC code, value added, waste treatment
(2) waste properties - form, physical properties, economic and planning data
(3) ultimate waste composition (if wastes combined) - material codes
(4) intermediate wastes (each process) - water content, recovery value
(5) chemical classification - atomic number, density

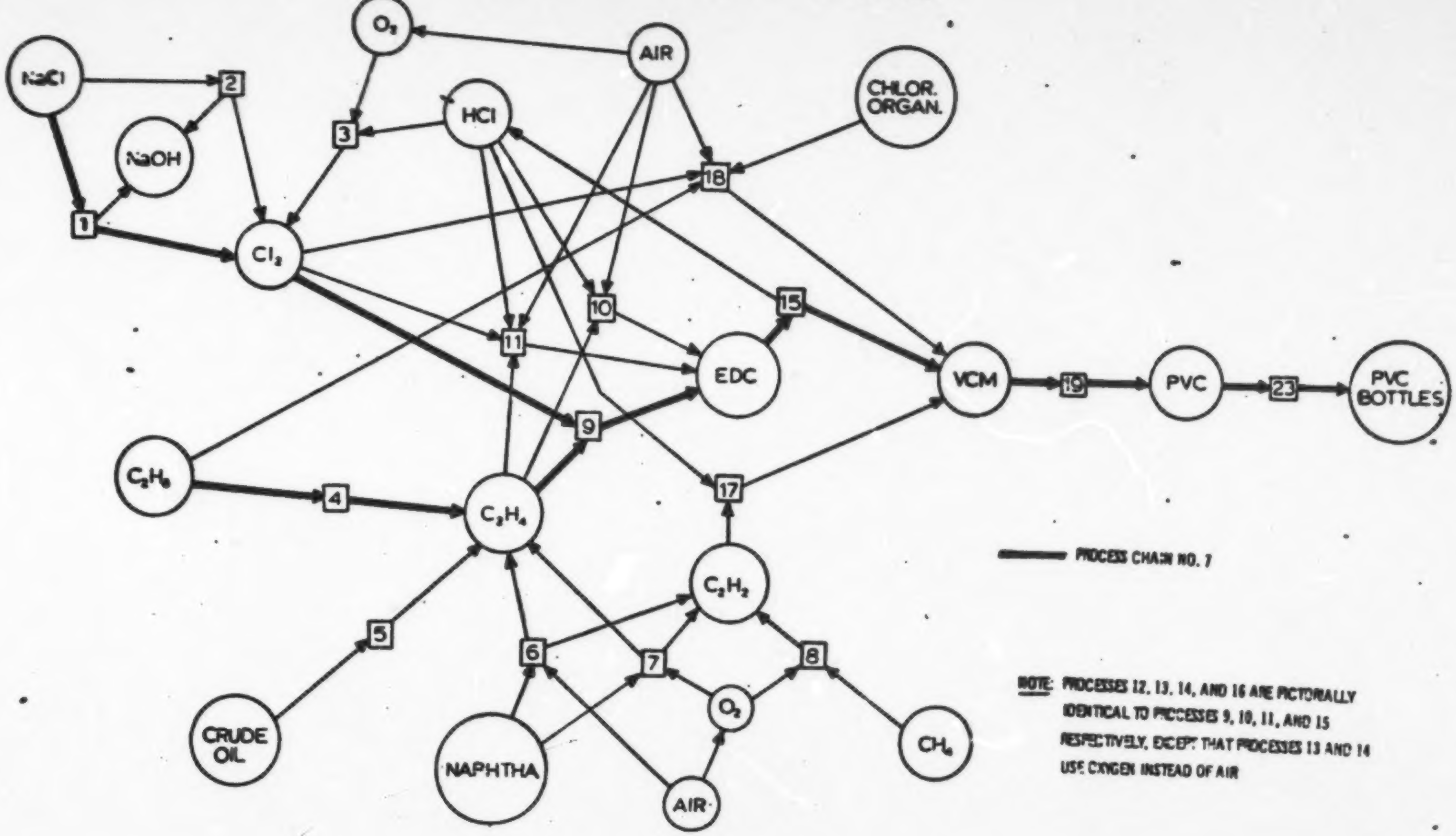
From such data, detailed planning for solid waste management can be conducted. Since information of this level of detail is beginning to be collected for air and water released wastes, its provision for solid wastes will enable construction of overall process (and industry) material balances. It seems realistic to expect that such an information system will be assembled in the next decade.

Under contract to the National Science Foundation, IR&T has developed a Materials-Process-Product (MPP) model which conducts material, energy, and economic balances over entire process chains.[65] A "process chain" is the sequence of material conversion steps that leads from the primary raw materials to the finished product. For example, a process chain leading to production of vinyl chloride monomer (VCM) might include: chlorine production via diaphragm cell electrolysis, ethylene production via ethane pyrolysis, ethylene dichloride (EDC) production by direct chlorination of ethylene, and VCM production by EDC pyrolysis. Another chain might employ mercury cell electrolysis for chlorine manufacture, and another replace ethane by naphtha as an ethylene feedstock. A network of process chains for polyvinyl chloride (PVC) bottles is shown in Figure 8, with the processes identified in Table 12. The objective of constructing such networks is to relate economic variables, such as market demand for PVC bottles, to materials and energy usages. When the entire economy has been so described, it will be possible to determine net requirements for a given material, e.g., sulfuric acid, and, likewise, net material wastes. At present, it is not feasible to gather the quantity and detail of information required for the entire economy, but the necessity to assemble such information for material planning purposes is rapidly increasing. The detail suggested by the ADL classification scheme is actually greater than required by the MPP model.

Another activity relevant to solid waste information management is work on an "Effluent Management Information System (EMIS) at Development Sciences Inc.[66] Like the IR&T model, EMIS employs a materials flow point of view. A regional data base for this model is now being established

FIGURE 8

PROCESS NETWORK LEADING TO PVC BOTTLES


NaCl
2
NaOH
1
Cl$_2$
O$_2$
3
HCl
AIR
CHLOR. ORGAN.
18
11
10
15
EDC
VCM
19
PVC
23
PVC BOTTLES
9
C$_2$H$_6$
4
C$_2$H$_4$
17
C$_2$H$_2$
5
6
7
8
O$_2$
CRUDE OIL
NAPHTHA
AIR
CH$_4$
PROCESS CHAIN NO. 7

NOTE: PROCESSES 12, 13, 14, AND 16 ARE PICTORIALLY IDENTICAL TO PROCESSES 9, 10, 11, AND 15 RESPECTIVELY, EXCEPT THAT PROCESSES 13 AND 14 USE OXYGEN INSTEAD OF AIR

TABLE 12

UNIT PROCESSES PARTICIPATING IN PVC BOTTLE MANUFACTURE

1. Chlorine via salt electrolysis - mercury cell
2. Chlorine via salt electrolysis - diaphragm cell

* 3. Chlorine via HCl oxidation using HNO_3 (Kel-Chlor)

4. Ethylene from ethane pyrolysis

* 5. Ethylene via autothermic cracking

6. Acetylene/ethylene via Wulff process (naphtha feed)

* 7. Acetylene/ethylene from naphtha by partial oxidation

8. Acetylene from methane by partial oxidation
9. EDC via ethylene chlorination (vapor)

*10. EDC via ethylene oxychlorination (vapor)

11. EDC via ethylene chlorination/oxychlorination (vapor)

*12. EDC via ethylene chlorination (liquid)

*13. EDC via ethylene oxychlorination (liquid)

*14. EDC via ethylene chlorination/oxychlorination (liquid)

15. VCM from EDC pyrolysis
16. VCM from EDC pyrolysis with waste treatment
17. VCM from concentrated acetylene

*18. VCM from ethane oxychlorination (Transcat) - part waste feed

19. PVC from VCM - bulk process.

23. PVC bottle manufacture

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*Processes not presently in domestic production.

for Southeastern Massachusetts. The objective of EMIS is to identify firms within and among industries which could benefit from resource recovery and shared capital investment in treatment centers. EMIS is designed to pose three questions:

(1) "Are there any chemicals or materials being captured in pollution control which can be used as raw materials by other processes?

(2) Are there any materials captured in pollution controls which can share treatment with other wastes?

(3) Are there any classified land ecosystems which can accumulate wastes with specified characteristics?"

Obviously, EMIS, like the MPP model, is limited by the extent of its data base.

VIII. WASTE TREATMENT AND DISPOSAL

This chapter considers the final stage in the materials processing sequence-waste treatment and disposal-in terms of present practice, environmental implications, and expectations for improved performance. The 33 selected chemicals are again used as a focus for discussion.

PRESENT DISPOSAL PRACTICE

Seven methods predominate among the alternatives for solid waste disposal. Considering each briefly:

(1) Incineration: This involves oxidative conversion of combustible solid material to harmless gases suitable for atmospheric release. Undesired gaseous products, such as HCl, SO_2, NO_x, must be removed prior to release. Heats of combustion may sometimes be recovered, and occasionally additional combustible material must be added to insure adequate combustion. Residual solids, i.e., ash, are landfilled. To the extent that residual solids remain, incineration is a waste reduction step rather than an ultimate disposal.

(2) Dispersal into contiguous water bodies: Historically, this practice has been widely employed, but EPA action has now curtailed it in many industries. Usually, the waste solid is temporarily stored in a lagoon, wherein it is treated to minimuze environmental impact. For example, acids and bases are neutralized and suspended solids are permitted to settle. In the case of river discharge, attempts are made to release the waste during periods of high flow.

(3) Ocean dumping: This practice involves transporting the material out to sea, then releasing it. Usually the material is conveyed by barge; it may be released directly or within containers. Costs depend upon the distance of transport, and

whether the material can be loaded in-plant or must be intermediately transported.

(4) Lagooning: Lagoons may be employed for either temporary or permanent storage. As previously mentioned, lagoons are frequently employed for interim storage and water treatment prior to release to contiguous water bodies. Permanent storage occurs when the solid material tends not to settle, e.g., phosphate slimes, or would have undesirable properties if water cover were not maintained, e.g., red mud (blows) from alumina and phossy water (burns) from phosphorus.[*]

(5) Sanitary landfill: This pertains to the burial of non-hazardous solid wastes under controls sufficient to preclude degradation of the surrounding environment. Controls include: proper site selection, exclusion of hazardous materials, periodic provision (usually daily) of soil cover, etc.

(6) Chemical landfill:[**] This is the extension of sanitary landfill to enable acceptance of hazardous materials. Included are: the provision of careful material identification, adequate safety standards (firefighting, etc.,), surface water channeling, leachate collection and treatment, materials recycling, etc.

(7) Subsurface injection: In this case the solid material is slurried and then pumped into underground cavities. The implications of many aspects of this practice are not yet clearly understood. Subsurface injection of hazardous waste should only occur when the leachate can be fully contained.

The unit costs of treatment via each of the seven techniques were ascertained from the literature. Actual costs vary widely depending upon waste quantity, geographic location, company size and expertise, etc. The values shown in Table 13 were employed in estimating the disposal

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[*] Phossy water is water which contains particles of phosphorus metal. The metal burns into flames when exposed to oxygen; thus water cover is required.

[**] Termed Class 1 landfill in California--no connection with groundwater.

TABLE 13

TREATMENT DISPOSAL COSTS

METHOD	COST ($/T)	QUALIFICATIONS
(1) Incineration	8[67]	HC still bottoms, slight inorganic content.
"	15[68]	high water, ash, sulfur, or chlorine content
"	95[69]	hazardous waste
(2) Dispersal to contiguous water	-	storage costs attributed to lagooning
(3) Ocean dumping	1-3[70,71]	excluding containment and transport
(4) Lagooning	1-3	
neutralization/ precipitation	10[72]	
(5) Sanitary landfill	3-5[73,74]	excluding inplant collection and storage
(6) Chemical landfill	40[75]	
(7) Disposal fee	19-82	quote from Rollins

costs for the 33 selected chemicals.* It was assumed that slurries and sludges are temporarily stored in lagoons pending final disposal, and that acids and bases are neutralized at that point. Hazardous wastes were relegated to chemical landfill. The disposal cost estimates are presented for each chemical in Table 6. This data has been aggregated by SIC Sector in Table 14. Two striking aspects of present disposal costs are:

(1) Sector 2819 accounts for 71% of total costs. As discussed below, our estimate may not fully account for the scale economics available with such large volume wastes.

(2) Organics do not pose a significant solid waste problem. Their disposal cost is less than 9% of the total.

The costs are lowest for Sector 2813. This is because there is only one solid waste producer in the sector- acetylene via the carbide process.

It is useful to place the disposal figures for the 33 chemicals in perspective. The total waste quantity from the 33 chemicals is calculated to be 55.9 million tons. This compares with an estimate of 140 million tons for all industrial solid wastes. The correspondence seems reasonable, in view of the high contribution from phosphorus and phosphoric acid solid wastes. In terms of disposal cost, the estimated $70.7 million for the 33 chemicals exceeds the $45.3 million** attributed to all chemical manufacture (Sectors 281 and 282) by the 137 corporate members of the Manufacturing Chemists Association.[76] There are four sources from which the discrepancy between these two estimates may arise:

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*Subsurface injection is not included since this is not the predominate disposal method for any of the wastes considered.

**IR&T estimate based on MCA data; includes all operating and maintenance costs plus 10% of original capital investment.

TABLE 14

SUMMARY OF SW TREATMENT AND DISPOSAL COSTS FOR 33 CHEMICALS

	Waste Amount (10^3 S.T.)	Present Disposal Cost ($1000)	Improved Disposal Cost ($1000)	Cost Ratio
Inorganics	55,024	64,963	121,501	1.87
2812	8,579	8,709	38,528	4.42
2813	589	1,178	2,945	2.50
2816	2,692	4,841	22,192	4.58
2819	43,164	50,235	57,836	1.15
Organics	1,491	5,750	19,967	3.47
2815	554	1,896	3,165	1.67
2818	937	3,854	16,802	4.36
Total	56,515*	70,713	141,468	2.00

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*Includes material sold as byproduct; such material (584 x 10^3 S.T.) is not included in cost estimates.

(1) the Manufacturing Chemists Association estiamte only includes expenditures by its members; these are the largest producers, however, and probably account for 99% of production;

(2) inaccuracies in our estimations of waste quantities are passed on in the estimation of disposal costs;

(3) some of the expense we have allocated to solid wastes may be considered within the category of water treatment by the MCA, e.g., acid neutralization; it is extremely difficult to eliminate such bookeeping type discrepancies;

(4) we have probably not fully accounted for existing scale economies; for example, $32.7 million of our estimate is traceable to phosphorus and phosphoric acid treatment, and operation at this level can probably be conducted at less than the $1/ton assumed; to illustrate, disposal of phosphate slurries at a Florida phosphate plant costs $0.245/ton[77]; if this figure is assumed to also apply to the phosphorus and phosphoric acid wastes*, our cost estimate is reduced by $24.7 million; this single change suffices to bring our estimate in line with that of the MCA.

It is felt that when the four factors are considered the correspondence between the two estimates is reasonable. Also, the manner in which our individual chemical estimates have been made is clearly evident, and so they furnish useful first estimates for use in further consideration of industrial chemical solid waste management costs.

Land usage requirements for disposal of solid wastes from the 33 chemicals are estimated in Table 15. This table accounts for the disposition of over 99% of the solid wastes. The remainder are incinerated or sold

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*Such low cost solid waste management was observed by the author (JCS) during a visit to Freeport Chemical's Uncle Sam (wet process) phosphoric acid plant.

TABLE 15

LAND USE FOR SOLID WASTE DISPOSAL

Storage or Disposal Mode	Waste Quantity (10^3 S.T.)	Waste Volume* (10^6 cu. yd.)	Land Area** (acres)
Temporary Lagooning	12,064	161	2,080
Permanent Lagooning	29,460	393	5,075
Sanitary Landfill	14,930	60	769
Chemical Landfill	217	1	11
	56,671	615	7,935***

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*Based on 504 lb./yd.^{3} and 30% solids content in lagoon.

**Based on 48 ft. depth for lagoons and landfills.

***This represents land used during the year. The 2080 acres employed for temporary lagooning can be reused. The remaining 5855 acres are added to permanent inventory.

as byproduct.* Lagooning accounts for 90% of the land use. This is traceable to its use in control of ore residuals, such as red mud, and for storage of large volume inorganic byproduct salts prior to their dispersal to water bodies. As noted in the table, 2080 acres are available for reuse and 5855 acres are added to permanent inventory. In comparison, 5 x 10^6 acres of land are presently occupied by the extractive industries, and roughly 5% of this figure, i.e., 250,000 acres, is consumed each year.[78] Industrial chemical annual land usage is, therefore, less than 3% that of the extractive industries. A significant factor is that, like the extractive industries, most industrial chemical facilities producing large quantities of solid waste are located in rural areas, e.g., phosphorus and phosphoric acid plants. When this is not the case, as for carbide-process acetylene manufacture, solid waste disposal land requirements do pose a problem.

ENVIRONMENTAL CONSIDERATIONS

The environmental problems associated with present disposal methods can be described in terms of the seven techniques which now predominate. Considering the environmental implications of each:

(1) Incineration: Unless adequate controls are exercised, incineration can lead to atmospheric release of undesired materials. The increasing stringency of air pollution regulations is leading to more expensive, environmentally acceptable practice in most instances. For example, hydrogen chloride generated during incineration of chlorinated hydrocarbons is now being removed through absorption in water. The hydrochloric acid so formed is then either neutralized or is concentrated for

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*The estimate for chemical landfill assumes most tars are handled in this manner. Since tars are incinerated whenever possible, the land requirements for chemical landfill may be overestimated. However, Union Carbide's Institute, West Virginia plant, alone allocates 24,000 cu. yds. per year to chemical landfill.

plant use.

(2) Dispersal into contiguous water bodies: If water salinity is unduely increased, water biota are endangered and ultimately agricultural land is harmed. Interim water pollution regulations are acting to curtail discharge of dissolved solids. Most firms are preparing to lagoon material previously discharged.

(3) Ocean dumping: There have been a number of instances of fish kill and beach spoilages due to ocean dumping. The Marine Protection, Research, and Sanctuaries Act of 1972 establishes a permit system for control of future ocean dumping. In addition, the Secretary of Commerce has been instructed to conduct and encourage a broad effort aimed at minimizing or ending all dumping of materials within five years of the effective date of the act (23 October 1973).

(4) Lagooning: Potential environmental problems that may result from lagooning relate to subsurface transport of the leachate and surface water runoff. For example, during the rainy season lagoons may overflow, and occassionally the containment dikes are breached. Such an instance is reported in EPA's Report to Congress on Hazardous Waste Disposal:

> "Phosphate Slime Spill. On December 7, 1971, at a chemical plant site in Fort Meade, Florida, a portion of a dike forming a waste pond ruptured releasing an estimated two billion gallons (7.58 billion liters) of slime composed of phosphatic clays and insoluble halides into Whidden Creek. Flow patterns of the creek led to subsequent contamination of Peace River and the estuarine area of Charlotte Harbor. The water of Charlotte Harbor took on a thick milky white appearance. Along the river, signs of life were diminished, dead fish were sighted and normal surface fish activity was absent. No living organisms were found in Whidden Creek downstream of the spill or in Peace River at a point eight miles downstream of Whidden Creek. Clam and crab gills were coated with the milky substance and in general all benthic aquatic life was affected in some way."[79]

(5) Sanitary landfill: Sanitary landfill protects against surface runoff but the concern remains that the leachate may cause environmental damage. For this reason, hazardous wastes cannot be accommodated in such a facility. The potential duration of danger from leachate is illustrated by the following experience.[80]

> "As a result of arsenic burial 30 years ago on agricultural land in Perham, Minnesota, several people who recently consumed water contaminated by the deposit were hospitalized. The water came from a well that was drilled near this 30 year old deposit of arsenic material. Attempts to correct this contamination problem are now being studied."

(6) Chemical landfill: If properly managed, this method of disposal poses no environmental hazard. Care must be taken to contain contaminated surface runoff and leachate.

(7) Subsurface disposal: The dangers with this technique are that large quantities of material may be emplaced before difficulties arise. EPA opposes such disposal practice for hazardous wastes,[81]

> "unless all other alternatives have been found to be less satisfactory in terms of environmental protection, and unless extensive hydraulic and geologic studies are made to insure that ground water contamination will be minimized".

The overall effect of environmental considerations for the seven disposal techniques is to identify incineration, sanitary landfill, and chemical landfill as the preferred modes of disposal. Those alternatives which lead to dispersal in water bodies will be increasingly curtailed. Lagooning will be continued for temporary storage and in those cases in which it is not possible to convert the waste to a form suitable for ultimate emplacement or destruction. Subsurface disposal may ultimately become established as a viable alternative for non-hazardous wastes as more experience is gained in this technique. In the next section we consider the effect of increased land disposal on the costs of waste disposal for Sector 281.

IMPROVED DISPOSAL PRACTICE

The treatment and disposal costs were re-evaluated in light of the expected changes in solid waste management. The costs of such improved treatment are given by chemical in Table 6 and by SIC Sector in Table 14. The costs for the 33 chemicals were determined to be double those of present treatment. In effect, it can be said that the solid waste disposal portion of the "costs of clean water" for these chemicals is $70.7 million. The inorganics continue to account for over 90% of the total cost, with Sector 2819 remaining the largest contributor. Sector 2819's contribution diminishes from 72% to 41%, however. This because disposal techniques will not change greatly for this sector, the principal difference being more rapid utilization of low cost, rural land for permanent lagooning.

The cost ratios in Table 14 serve to highlight areas in which non-typical changes occur. The absence of significant change in Sector 2819 has already been discussed. In contrast, sectors 2812, 2816, and 2818 exhibit higher than average cost increases. In Sector 2812 all of the chemicals exhibit a significant cost increase. Principal sources of increase are the chemical landfilling of treated mercury-containing sludges (from chlorine-caustic production) and the sanitary landfilling of the Solvay plant calcium chloride waste (due to inadequate market demand for this byproduct). In Sector 2816 the increased rate stems directly from the necessity for improved treatment of acid sludges from the sulfate process for titanium dioxide. To the extent that resource recovery and process change occur, as discussed in the case study, this cost increase may be reduced. In Sector 2818 the high cost increase is again attributable to a single source - the necessity to provide ultimate disposal for alkyl lead wastes. Market decline (for environment-related reasons) is causing a reduction of alkyl lead wastes. Present considerations regarding hazardous waste handling will determine the disposition of such wastes. Land usage for solid wastes from the 33 chemicals following curtailment of water discharge is shown in Table 16. At present, material temporarily stored in lagoons is subsequently discharged to the river, ocean dumped, or sent to sanitary landfill. About 760 x 10^3 S.T. are estimated to fall into the latter category, with the remaining 11,300 S.T. discharged to water bodies. It was assumed that when discharge to water bodies is curtailed, half the material now temporarily stored in lagoons will be retained in permanent lagoons and the remainder will be consolidated in landfill. Comparing Tables 15 and 16 we see that land use actually decreases. This is due to the consolidating effect of solids transfer from lagoons to sanitary landfill. Land consumption increases by 22%, however, since the land becomes the final repository of material previously released to the water bodies. Nevertheless, land consumption remains a small percentage of that for the extractive industries.

TABLE 16

LAND USE FOR SOLID WASTE DISPOSAL IN ABSENCE OF WATER DISCHARGE

Storage or Disposal Mode	Waste Quantity (10^3 S.T.)	Waste Volume* (10^6 cu. yd.)	Land Area** (acres)
Permanent Lagooning	35,110	468	6053
Sanitary Landfill	20,580	82	1062
Chemical Landfill	217	1	11
Other	24	----	-----
	55,931***	551	7126

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*Based on 504 lb./yd.^{3} and 30% solids content in lagoon.

**Based on 48 ft. depth for lagoons and landfills.

***Another 584 x 10^3 S.T. are sold as byproduct (refer Table 11.)

IX. GOVERNMENTAL OPPORTUNITIES TO INFLUENCE THE MANAGEMENT OF INDUSTRIAL CHEMICAL SOLID WASTES

In previous chapters we have addressed present practice for resource recovery and waste disposal of industrial chemical solid wastes. We have predicted changes to the solid waste stream that will result from ongoing and anticipated process changes, and evaluated the effect of changes in waste disposal that have been motivated by constraints on water disposal. In this chapter we consider in what way the government might contribute to improved waste management in the industrial chemicals sector either in the form of increased resource recovery or enhanced disposal methods. First we place such opportunities in perspective by considering the industry's capability and responsiveness to improved waste management, and the activity already being pursued by the government. We then consider additional opportunities for governmental action.

PERSPECTIVE

The character of the industry itself is the most important factor bearing upon the need for and appropriate extent of governmental incursion into the workings of a commercial sector. When changes to present practice are sought, the specific factors to be considered are the industry's capability to accomplish the desired change and its responsiveness to the need for the change. Industrial chemical manufacturers have demonstrated their capability to institute changes when economic conditions dictate. Further, to date they have been relatively responsive to the increasingly stringent controls being placed upon their interaction with the environment. Although there have been notable exceptions, industry has generally succeeded in meeting the deadlines set for process waste control. The desire to maintain good public relations serves as an important prod for heeding rather than hindering calls for improved environmental practice.

The industrial chemical industry is highly competitive, and as a result individual companies must be adaptive to market forces. A reflection of this adaptability can be seen in the many process substitutions which occur. Those pertaining to the 33 selected chemicals are summarized in Table 17.* As indicated, nearly half of the selected chemicals are undergoing process substitutions. In every instance the process substitution leads to a reduction in solid waste genration. Although other economic factors play a role, it is evident that the industry is already responding to pollution reduction constraints. In addition to displaying a capability for realignment, the financial capacity to completely eliminate product lines, such as chlorinated pesticides, has been demonstrated.

The foregoing discussion leads to the conclusion that the industry possesses a capability at least equal to that of government to translate environmental prerequisites into economic decisions. In light of this it seems most appropriate for the governmental strategy to center around the identification and regulation of environmental prerequisites. In the area of solid wastes this means the preservation of scarce resources and the insurance of proper residuals disposal.

Government intervention to preserve scarce resources seems justified only when market forces fail to do so. We have not identified any instances in which industry has failed to attempt recovery of a scarce resource. Two examples are the steps being taken to recover the

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*These process substitutions were discussed in the chapter on market and process changes. Their effect on solid waste was appraised. Projections were made for the years 1977 and 1982.

TABLE 17

PROCESS CHANGE AMONG THE 33 SELECTED CHEMICALS

SIC CODE	CHEMICAL PRODUCED	SUBSTITUTION* TIMING	SUBSTITUTEE	SUBSTITUTOR
2812	Chlorine/Sodium hydroxide	0	mercury cell	diaphragm cell
	Sodium Carbonate	0	Solvay process	natural ore
2813	Acetylene	0	carbide process	hydrocarbon conv.
2815	Benzene	0	coal tar	petroleum
	Phenol	0	benzene sulfon.	cumene oxidation
2816	Titanium dioxide	0	sulfate process	chloride process
2818	Chloroform	P	acetone bleaching	chlorination
	Ethylene oxide	P	chlorohydrin	direct oxidation
	Glycerine	0	natural	synthetic
	Perchloroethylene	0	acetylene	hydrocarbon chlor.
	Propylene oxide	0	chlorohydrin	Oxirane process
2819	Alumina	F	Bayer Process	Troth process
	Hydrochloric acid	0	acid/salt	byproduct
	Hydrofluoric acid	F	fluorspar	phosphoric acid waste

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*Timing of Substitution: past (P), on going (0), future (F) fluorine from phosphoric acid sludges and the alumina, titanium dioxide, and iron content of the red mud from bauxite. Fluorine reserves are low and both aluminum and titanium are valuable metals. In both cases, the government has conducted extensive research programs, but it is not clear to what extent the government's program has been synergistic with that of industry. One particular aspect to be considered in the preservation of scarce resources is that wastes be discarded in such a manner that future resource recovery is neither precluded nor made unresonably difficult. An obvious step in this direction is the curtailment of waste disposal through dilution in large water bodies, i.e., rivers and oceans. Action toward this end is already being taken from the standpoint of maintaining proper water quality. It will have the corollary effect of maintaining the potential for resource recovery from industrial chemical solid wastes even after they are allocated to (land) disposal.

The government is already active in the insurance of proper residuals disposal. Water discharge controls have motivated the process substitutions shown in Table 17 for chlorine, sodium hydroxide, sodium carbonate, and titanium dioxide. Similar regulation of solid waste disposal is now receiving attention. EPA's Office of Solid Waste Management Programs has in 1973 promulgated proposed guidelines for sanitary landfill and reported to Congress on alternatives for hazardous waste disposal.[82] The results achieved in the amelioration of air and water pollution demonstrate the efficiency of such a regulatory approach. This is recognized as the most important step the government can take to ensure proper environmental management. In the following section, additional opportunities for the governmental insurance of proper management of industrial chemical solid wastes are discussed.

APPRAISAL OF GOVERNMENTAL STRATEGY OPTIONS

We consider governmental strategy options as falling within six general categories: regulations, tax incentives, subsidies, preferential procurement, research and development, and public education. In the following paragraphs we present steps the government might take in control of industrial chemical solid wastes that go beyond the current effort related to sanitary landfill and hazardous waste disposal.

Regulation

The two steps that we recommend be undertaken in the regulation of industrial chemical solid wastes are:

(1) require documentation of the quantity and chemical composition of the process-related solid waste load from each production facility, and

(2) impose and enforce standards for disposal via lagoons and subsurface injection comparable to those being prepared for sanitary landfill and hazardous waste disposal.

Documentation of the content of water borne wastes is already required for critical components, e.g., phosphates, prior to the issuance of a discharge permit. Similar information on solid wastes would enable the assurance of proper disposal, assist in the planning of future disposal modes, and permit the monitoring of significant resources. Plant-wide identification of waste stream content may be all that is required, although as indicated in this report process-specific identification of wastes is necessary in order to predict future changes to the waste stream.

There is already governmental activity in the area of improved lagooning and subsurface injection practice. For example, the Bureau of Mines has investigated various modes of sludge dewatering: chemical,[83] mechanical, vegetative,[84] etc. The Bureau has also investigated various aspects of subsurface disposal. We recommend that EPA place emphasis on understanding the basic prerequisites of each of these waste management techniques from the standpoint of avoiding both short and long term environmental degradation.

Alternative opportunities for regulation of industrial chemical solid wastes which we have considered include: legislation of a particular resource recovery technique, outlawing of production processes that generate excessive amounts of pollutants, or imposition of import restrictions to motivate use or recovery of domestic resources. At this stage in the imposition of solid waste controls, none of these specific constraints on the commercial process seems appropriate. Rather, proper environmental constraints are required, with the development of an information system and enforcement machinery to insure compliance with these constraints.

Tax Incentives

Tax incentives that might be cmployed could range from accelerated depreciation of equipment intended for enhanced resource recovery or residuals disposal to impositions of graduated tax penalties for failure to achieve specified norms of disposal. Alternatively, a deadline could be set for achieving a specific discharge standard, and tax incentives offered for earlier achievement of the given standard. We do not recommend such tax strategies. Processes that produce disproportionately large wastes may be inexpensive precisely because waste disposal practices are inadequate. When this is true, tax incentives will be ineffective unless calibrated with greater precision than taxing procedures permit. Direct regulation seems preferable.

Subsidy

It is our premise that only in the event a specific resource needs to be conserved should direct or indirect subsidies be provided. Otherwise, the government ends up paying for a change that would ultimately be made at no cost via economic adjustments. In our study of the 33 selected chemicals we have identified no instances in which subsidies should be provided.

Temporary subsidies were considered directed toward the recovery or disposal process itself. For example, part of the start-up cost of improved disposal might temporarily be subsidized by the government. However, we have not encountered evidence that such subsidies are necessary. The existence of companies, such as Rollins Environmental Services, that provide disposal service at a fee would seem to offer an interim solution for a firm needing time to develop its own technology.

Preferential Procurement

Three variations of preferential procurement have been considered: Selective purchase of recovered materials from U.S. firms or purchase of primary products only from firms that have been actively complying with feasibly established solid waste disposal standards. In the first case, the need for action to promote resource recovery has not been identified among the chemicals of Sector 281. In terms of reward or penalty to ameliorate unsatisfactory disposal procedures, selective procurement seems an administratively cumbersome substitute for direct regulation.

Research and Development

This is an area in which the government is already active. Programs are underway in a number of areas: sludge dewatering, appraisal of deep well disposal, assessment of long term environmental implications of present practice. The emphasis here, as in other areas, should be in the definition of the standard to be met, while leaving to industry the development of the technology to meet the standard. Work to be supported is that necessary to permit regulation of lagooning and subsurface disposal and to complete the ongoing definition of ocean dumping, sanitary landfill, and hazardous waste disposal standards.

Public Education

Two areas of public education might be amplified:

(1) if, as seems presently the case, industry is cooperating with government in the attainment of environmental objectives, this cooperation should be brought to public attention, and

(2) when consumer pressure can be used to motivate more rapid achievement of a particular goal, public education could be usefully employed to elucidate the alternatives.

To summarize the foregoing, the principal action of the government in the area of industrial chemical solid wastes should be toward improved, environmentally based, regulation of disposal methods. This conclusion is based on the premise that this highly competitive industry is itself best suited to judging the paths whereby the environmental objectives are to be achieved.

X. LIST OF REFERENCES

I. INTRODUCTION

1. Annual Survey of Manufactures, U.S. Bureau of the Census, 1970.

2. "Solid Waste Management in the Industrial Chemical Industry", The Research Corporation of New England [SW-33c] for EPA, 1971. [Draft]

3. Faith, W.L., Keyes, D.B., and Clark, R.L., Industrial Chemicals, 3rd ed., John Wiley and Sons, New York, 1965.

4. Kirk, R.E., and Othmer, D.F., Encyclopedia of Chemical Technology, Volume 1-25, John Wiley & Sons, New York, 1963-1972.

5. Shreve, R.N., "The Chemical Process Industries", 2nd ed., McGraw-Hill Book Company, New York, 1956.

6. "Inorganic Chemicals Industry Profiles", Datagraphics Inc. for EPA [#12020 EJI], Gov't. Printing Office, July 1971.

7. "Projected Wastwater Treatment Costs in the Organic Chemical Industry", Datagraphics Inc. for EPA [#12020 GWD], Gov't. Printing Office, July 1971.

8. "Industrial Waste Study of Inorganic Chemicals, Alkalies and Chlorine", General Technologies Corp. for EPA [#68-01-0020], 23 July 1971. [Draft]

9. "A Study of Hazardous Waste Materials, Hazardous Effects and Disposal Methods", Booz Allen Applied Research Inc. for EPA [#68-03-0032], June 1972.

10. "Recommended Methods of Reduction, Neutralization, Recovery and Disposal of Hazardous Waste", TRW for EPA [#68-03-0089], Feb. 1973 [Draft]

11. "Program for the Management of Hazardous Wastes", Battelle Memorial Institute for EPA [#68-01-0762] March 1973.

12. "Alternatives to the Management of Hazardous Wastes at National Disposal Sites", ADL for EPA [#68-01-0556], May 1973. [Draft]

13. Mineral Facts and Problems, U.S. Dept. of the Interiors, 1970.

14. *Minerals Yearbook* (Vol. II), U.S. Dept. of the Interior, 1970.

15. "1971 Directory of Chemical Producers, USA", Stanford Research Institute, Calif., 1971.

16. Backman, J. "The Economics of the Chemical Industry", Manufacturing Chemists Association, Washington, D.C., Feb. 1970.

17. "Chemical Statistical Handbook", 7th ed., Manufacturing Chemists Association, Washington, D.C., 1971.

18. Ibid.

19. Brownstein, A.M., Spitz, P.H., Springborn, R.C., "Changes in Technology and Products Anticipated by 1985", in *The Changing World Chemical Industry. . .Its Outlook & Problems to 1985*. Manufacturing Chemists Association, Washington, D.C., 1973.

IV. INUDSTRIAL CHEMICAL SOLID WASTE GENERATION

20. Op. cit., reference 3.

21. Op. cit., reference 2.

22. George Hanks, Union Carbide, personnel communication.

23. Op. cit., reference 3.

24. Ibid.

25. Op. cit., reference 4.

26. Op. cit., reference 6.

27. Op. cit., reference 7.

28. Op. cit., reference 8.

29. Op. cit., reference 9.

30. Op. cit., reference 10.

31. Op. cit., reference 11.

32. Op. cit., reference 12.

33. Op. cit., reference 13.

34. Op. cit., reference 14.

35. Chemical and Engineering News, 22 January 1973, pp. 8-9.

36. "Utilization of Waste Fluosilicic Acid", U.S. Dept. of the Interior [RI 7502], April 1971.

37. "Phosphate-Plant Waste Looms As Hydrofluoric-acid Source", Chem. Eng., May 4, 1970, pp. 46-48.

38. "At the ready: New Routes to Hydrofluoric Acid", Chemical Week, Vol. 108 No. 1 (Jan. 6, 1971) pp.47-50.

39. G. C. Brown and D. C. Harper, Patent No. 1,179,246 (Jan. 28, 1970).

V. INDUSTRIAL CHEMICAL SOLID WASTE DATA BASE

40. "Chemical Origins and Markets" Stanford Research Institute, California, 1969.

41. Chemical Engineering . McGraw-Hill Publication (bi-weekly).

42. Chemical Engineering Progress. Published by American Institute of Chemical Engineers (monthly).

43. Chemical Week. Published by McGraw-Hill, Inc. (weekly).

44. Chemical and Engineering News. Published by the American Chemical Society. (weekly)

IV. MARKET AND PROCESS CHANGE EFFECTS ON SOLID WASTE GENERATION

45. "Processes for Rutile Substitutes", National Materials Advisory Board [NMAB-293] for the National Academy for Science, June 1972. p. 28

46. Ibid.

47. "Cyanamid Proposes Alternative to Ocean Dumping of Waste Water", Chemicology (Published by Manufacturing Chemists Association), Feb. 1973.

48. Op. cit., reference 22.

49. Chemical Week, March 7, 1973, p. 40

50. Chemical Week, August 9, 1973, p. 32

51. Op. cit., reference 2, p. 164.

52. Chemical and Engineering News, August 3, 1970.

53. Chemical and Engineering News, Feb. 26, 1973, p. 11.

VII. RESOURCE RECOVERY NEEDS AND OPPORTUNITIES

54. "Exploratory Study on Alternative Pollution Abatement Techniques Through Continued Development of the Ecosystem of Machines Information System", Development Sciences Inc. for NSF (c-673), July 17, 1972.

55. "Industrial Solid Waste Classification" Arthur D. Little, Inc., for EPA (#68-03-0123), December 1972 [Draft]

56. Frantz, J. "Byproduct processing, Theres Gold on Them Thar Streams" presented to the American Institute of Chemical Engineers, March 12, 1973.

57. "Phosphoric Acid: Electrothermal vs. Wet Process" The Sulfur Institute, Washington D. C., April 1969, p. 11. [723.0000-762.9999]

58. Chemical Economic Handbook, Stanford Research Institute, 1969, p. 761.5020 D

59. Op. cit., reference 13, p. 1044.

60. Ibid.

61. Ibid.

62. Op. cit., reference 36.

63. Op. cit., reference 56.

64. Op. cit., reference 55.

65. Ayres, R., Saxton, J., Stern, M. "Materials-Process-Product Model for the Bottle Manufacturing Industry for NSF [NSF-C 652], Dec. 1972.

66. Op. cit., reference 54.

VIII. WASTE TREATMENT AND DISPOSAL

67. Op. cit., reference 55.

68. Ibid.

69. "Report to Congress on Hazardous Waste", Office of Solid Waste Management Programs, EPA Hazardous Waste Section, Washington, D. C., June 30, 1973.

70. Ibid.

71. Chemical Engineering Deskbook, August 1972.

72. Op. cit., reference 69.

73. Ibid.

74. Op. cit., reference 71.

75. Slover, Edwin E., "Solid Waste Disposal in a Multi-Product Chemicals Plant", for the American Association of Textile Chemists and Colorists Symposium; The Textile Industry and the Environment-1973, Washington, D.C., May 22-24, 1973.

76. "Environmental Commitment-1972", Manufacturing Chemists Association, 1972.

77. "Waste Disposal Costs of a Florida Phosphate Operation", Bureau of Mines Information Circular 8404, 1969.

78. Stern, Martin, "S.E.A.S. Test Model: Land Use Forecasts," Prepared for EPA, 1973, IRT-314-R.

79. Op. cit., ref. 69.

80. Ibid.

81. Ibid.

IX. GOVERNMENTAL OPPORTUNITIES TO INFLUENCE THE MANAGEMENT OF INDUSTRIAL CHEMICAL SOLID WASTES

82. Op. cit., reference 69.

83. "Chemical Stabilization of the Uranium Tailings at Tuba City, Arizona" Bureau of Mines report of Investigation 7288, 1969.

84. "Chemical and Vegetative Stabilization of a Nevada Copper Porphysy Mill Tailing" Bureau of Mines REport of Investigation, 7261, May 1969.

XI. PENDING PUBLICATIONS

The report has been submitted to Chemical Engineering. A review of the study will be published.

XII. APPENDIX

Major Group 28.—CHEMICALS AND ALLIED PRODUCTS

The Major Group as a Whole

This major group includes establishments producing basic chemicals, and establishments manufacturing products by predominantly chemical processes. Establishments classified in this major group manufacture three general classes of products: (1) basic chemicals such as acids, alkalies, salts, and organic chemicals; (2) chemical products to be used in further manufacture such as synthetic fibers, plastics materials, dry colors, and pigments; (3) finished chemical products to be used for ultimate consumption such as drugs, cosmetics, and soaps; or to be used as materials or supplies in other industries such as paints, fertilizers, and explosives. The mining of natural rock salt is classified in mining industries. Establishments primarily engaged in manufacturing nonferrous metals and high percentage ferroalloys are classified in Major Group 33; silicon carbide in Major Group 32; baking powder, other leavening compounds, and starches in Major Group 20; and embalming fluids and artists' colors in Major Group 39. Establishments primarily engaged in packaging, repackaging, and bottling of purchased chemical products, but not engaged in manufacturing chemicals and allied products, are classified in trade industries.

Group No. Industry No.

281 INDUSTRIAL INORGANIC AND ORGANIC CHEMICALS

This group includes establishments primarily engaged in manufacturing basic industrial inorganic and organic chemicals. Establishments primarily engaged in manufacturing formulated agricultural pesticides are classified in Industry 2879; organic and inorganic medicinal chemicals, drugs and medicines in Industry 2833; wood distillation products and naval stores in Group 286; and soap, glycerin (except synthetic), and cosmetics in Group 284.

2812 Alkalies and Chlorine

Establishments primarily engaged in manufacturing alkalies and chlorine.

Alkalies
Carbonates, potassium and sodium
Caustic potash
Caustic soda
Chlorine, compressed or liquefied
Potassium carbonate
Potassium hydroxide
Sal soda
Soda ash
Sodium bicarbonate
Sodium carbonate (soda ash)
Sodium hydroxide (caustic soda)

2813 Industrial Gases

Establishments primarily engaged in manufacturing gases for sale in compressed, liquid, and solid forms. Establishments primarily engaged in manufacturing fluorine, ammonia, and sulfur dioxide are classified in Industry 2819; and chlorine in Industry 2812. Distributors of industrial gases and establishments primarily engaged in shipping liquid oxygen are classified in trade.

Acetylene
Argon
Carbon dioxide
Dry ice (solid carbon dioxide)
Gases, industrial: compressed, liquefied, or solid—not made in petroleum refineries or in natural gasoline plants
Helium
Hydrogen
Neon
Nitrogen
Nitrous oxide
Oxygen, compressed and liquefied
Refrigerant gases, except ammonia

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Group No. Industry No.

281 INDUSTRIAL INORGANIC AND ORGANIC CHEMICALS—Continued

2815 Cyclic Intermediates, Dyes, Organic Pigments (Lakes and Toners), and Cyclic (Coal Tar) Crudes

Establishments primarily engaged in manufacturing cyclic organic intermediates, dyes, color lakes and toners, and coal tar crudes. Important products of this industry include: (1) derivatives of benzene, toluene, naphthalene, anthracene, pyridine, carbazole, and other cyclic chemical products; (2) synthetic organic dyes; (3) synthetic organic pigments; and (4) cyclic (coal tar) crudes, such as light oils and light oil products; coal tar acids; and products of medium and heavy oil such as creosote oil, naphthalene, anthracene, and their higher homologues, and tar. Establishments primarily engaged in manufacturing coal tar crudes in chemical recovery ovens are classified in Industry 3312, and petroleum refineries which produce such products in Industry 2911.

Acid dyes, synthetic
Acids, coal tar: derived from coal tar distillation
Alkylated diphenylamines, mixed
Alkylated phenol, mixed
Aminoanthraquinone
Aminoazobenzene
Aminoazotoluene
Aminophenol
Aniline
Aniline oil
Anthracene
Anthraquinone dyes
Azine dyes
Azobenzene
Azo dyes
Azoic dyes
Benzaldehyde
Benzene hexachloride
Benzene, product of coal tar distillation
Benzoic acid
Benzol, product of coal tar distillation
Biological stains
Chemical indicators
Chips and flakes, naphthalene
Chlorobenzene
Chloronaphthalene
Chlorophenol
Chlorotoluene
Coal tar acids, derived from coal tar distillation
Coal tar crudes, derived from coal tar distillation
Coal tar distillates
Coal tar intermediates
Color lakes and toners
Color pigments, organic: except animal black and bone black
Colors, dry: lakes, toners, or full strength organic colors
Colors, extended (color lakes)
Cosmetic dyes, synthetic
Cresols, product of coal tar distillation.
Creosote oil, product of coal tar distillation
Cresylic acid, product of coal tar distillation
Cyclic crudes, coal tar: product of coal tar distillation
Cyclic intermediates
Cyclohexane
Diphenylamine
Drug dyes, synthetic
Dyes, synthetic organic
Eosine toners
Ethylbenzene
Food dyes and colors, synthetic
Hydroquinone
Isocyanates
Lake red C toners
Lithol rubine lakes and toners
Maleic anhydride
Methyl violet toners
Naphtha, solvent: product of coal tar distillation
Naphthalene, product of coal tar distillation
Naphthol, alpha and beta
Naphtholsulfonic acids
Nitroaniline
Nitrobenzene
Nitro dyes
Nitrophenol
Nitroso dyes
Oils: light, medium, and heavy—product of coal tar distillation
Orthodichlorobenzene
Paint pigments, organic
Peacock blue lake
Pentachlorophenol
Persian orange lake
Phenol
Phloxine toners
Phosphomolybdic acid lakes and toners
Phosphotungstic acid lakes and toners
Phthalic anhydride
Phthalocyanine toners
Pigment scarlet lake
Pigments, organic: except animal black and bone black
Pitch, product of coal tar distillation
Pulp colors, organic
Quinoline dyes
Resorcinol
Scarlet 2 R lake
Stilbene dyes
Styrene
Styrene monomer
Tar, product of coal tar distillation
Toluene, product of coal tar distillation.
Toluol, product of coal tar distillation
Toluidines
Toners (reduced or full strength organic colors)
Vat dyes, synthetic
Xylene, product of coal tar distillation
Xylol, product of coal tar distillation

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281 INDUSTRIAL INORGANIC AND ORGANIC CHEMICALS—Continued

2816 Inorganic Pigments

Establishments primarily engaged in manufacturing inorganic pigments. Important products of this industry include black pigments (except carbon black, Industry 2895), white pigments and color pigments. Organic color pigments, except animal black and bone black, are classified in Industry 2815.

Animal black
Barium sulfate, precipitated (blanc fixé)
Barytes pigments
Blanc fixé (barium sulfate, precipitated)
Bone black
Chrome pigments: chrome green, chrome yellow, chrome orange, zinc yellow
Color pigments, inorganic
Inorganic pigments
Iron blue pigment
Iron colors
Iron oxide, black
Iron oxide, magnetic
Iron oxide, yellow
Lamp black
Lead oxide pigments
Lead pigments
Litharge
Lithopone
Metallic pigments, inorganic
Mineral colors and pigments
Minium (pigment)
Ochers
Paint pigments, inorganic
Pearl essence
Pigments, inorganic
Prussian blue pigments
Red lead pigment
Satin white pigment
Siennas
Titanium pigments
Ultramarine pigment
Umbers
Vermilion pigment
White lead pigments
Whiting
Zinc oxide pigments
Zinc pigments: zinc yellow and zinc sulfide

2818 Industrial Organic Chemicals, Not Elsewhere Classified

Establishments primarily engaged in manufacturing industrial organic chemicals, not elsewhere classified. Important products of this industry include: (1) non-cyclic organic chemicals such as acetic, chloroacetic, adipic, formic, oxalic and tartaric acids and their metallic salts; chloral, formaldehyde and methylamine; (2) solvents such as amyl, butyl, and ethyl alcohols; methanol; amyl, butyl and ethyl acetates; ethel ether, ethylene glycol ether and diethylene glycol ether; acetone, carbon disulfide and chlorinated solvents such as carbon tetrachloride, perchloroethylene and tricholoethylene; (3) polyhydric alcohols such as ethylene glycol, sorbitol, pentaerythritol, synthetic glycerin; (4) synthetic perfume and flavoring materials such as coumarin, methyl salicylate, saccharin, citral, citronellal, synthetic geraniol, ionone, terpineol, and synthetic vanillin; (5) rubber processing chemicals such as accelerators and antioxidants, both cyclic and acyclic; (6) plasticizers, both cyclic and acyclic, such as esters of phosphoric acid, phthalic anhydride, adipic acid, lauric acid, oleic acid, sebacic acid, and stearic acid; (7) synthetic tanning agents such as naphthalene sulfonic acid condensates; (8) chemical warfare gases; and (9) esters, amines, etc. of polyhydric alcohols and fatty and other acids. Establishments primarily engaged in manufacturing plastic materials and nonvulcanizable elastomers are classified in Industry 2821; synthetic rubber in Industry 2822; essential oils in Industry 2899; wood distillation products, naval stores, and natural dyeing and tanning materials in Group 286; rayon and other synthetic fibers in Industries 2823 and 2824; specialty cleaning, polishing and sanitation preparations in Industry 2842; and paints in Industry 2851; organic pigments in Industry 2815; and inorganic pigments in Industry 2816. Distilleries engaged in the manufacture of grain alcohol for beverage purposes are classified in Industry 2085.

Accelerators, rubber processing: cyclic and acyclic
Acetaldehyde
Aetates, except natural acetate of lime
Acetic acid, synthetic
Acetic anhydride
Acetin
Acetone, synthetic
Acids, organic
Acrolein
Acrylonitrile
Adipic acid
Adiponitrile
Alcohol, aromatic
Alcohol, fatty: powdered

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281 INDUSTRIAL INORGANIC AND ORGANIC CHEMICALS—Continued

2818 Industrial Organic Chemicals, Not Elsewhere Classified—Continued

Alcohols, industrial: denatured (nonbeverage)
Algin products
Amines of polyhydric alcohols, and of fatty and other acids
Amyl acetate and alcohol
Antioxidants, rubber processing: cyclic and acyclic
Bromochloromethane
Butadiene, from alcohol
Butyl acetate, alcohol, and propionate
Butyl ester solution of 2, 4-D
Calcium oxalate
Camphor, synthetic
Carbon bisulfide (disulfide)
Carbon tetrachloride
Casing fluids, for curing fruits, spices, tobacco, etc.
Cellulose acetate, unplasticized
Chemical warfare gases
Chloral
Chlorinated solvents
Chloroacetic acid and metallic salts
Chloroform
Chloropicrin
Citral
Citrates
Citric acid
Citronellol
Coumarin
Cream of tartar
Cyclopropane
DDT, technical
Decahydronaphthalene
Dichlorodifluoromethane
Diethylcyclohexane (mixed isomers)
Diethylene glycol ether
Dimethyl divinyl acetylene (diisopropenyl acetylene)
Dimethylhydrazine, unsymmetrical
Enzymes
Esters of phthalic anhydride; and of phosphoric, adipic, lauric, oleic, sebacic, and stearic acids
Esters of polyhydric alcohols
Ethanol, industrial
Ether
Ethyl acetate, synthetic
Ethyl alcohol, industrial (nonbeverage)
Ethyl butyrate
Ethyl cellulose, unplasticized
Ethyl chloride
Ethyl ether
Ethyl formate
Ethyl nitrite
Ethyl perhydrophenanthrene
Ethylene
Ethylene glycol
Ethylene glycol ether
Ethylene glycol, inhibited
Ethylene oxide
Ferric ammonium oxalate
Flavors and flavoring materials, synthetic
Fluorinated hydrocarbon gases
Formaldehyde (formalin)
Formic acid and metallic salts
Freon
Fuel propellants, solid, organic
Fuels, high energy, organic
Gases, fluorinated hydrocarbon
Geraniol, synthetic
Glycerin, except from fats (synthetic)
Grain alcohol, industrial (nonbeverage)
Hexamethylenediamine
Hexamethylenetetramine
High purity grade chemicals, organic: refined from technical grades
Hydraulic fluids, synthetic base
Hydrazine
Industrial organic cyclic compounds
Ionone
Isopropyl alcohol
Ketone, methyl ethyl
Ketone, methyl isobutyl
Laboratory chemicals, organic
Lauric acid esters
Lime citrate
Malononitrile, technical grade
Metallic salts of acyclic organic chemicals
Metallic stearate
Methanol, synthetic (methyl alcohol)
Methyl chloride
Methyl perhydrofluorine
Methyl salicylate
Methylamine
Methylene chloride
Monochlorodifluoromethane
Monomethylparaminophenol sulfate
Monosodium glutamate
Mustard gas
Nitrous ether
Normal hexyl decalin
Nuclear fuels, organic
Oleic acid esters
Organic acids, except cyclic
Organic chemicals, acyclic
Oxalates
Oxalic acid and metallic salts
Pentaerythritol
Perchloroethylene
Perfume materials, synthetic
Phosgene
Phthalates
Plasticizers, organic: cyclic and acyclic
Polyhydric alcohols
Potassium bitartrate
Propellants for missiles, solid, organic
Propylene
Propylene glycol
Quinuclidinol ester of benzylic acid
Reagent grade chemicals, organic: refined from technical grades
Rocket engine fuel, organic
Rubber processing chemicals, organic: accelerators and antioxidants—cyclic and acyclic
Saccharin
Sebacic acid
Silicones
Soaps, naphthenic acid
Sodium acetate
Sodium alginate
Sodium benzoate
Sodium glutamate
Sodium pentachlorophenate
Sodium sulfoxalate formaldehyde
Solvents, organic
Sorbitol
Stearic acid esters
Stearic acid salts
Sulfonated naphthalene
Tackifiers, organic
Tannic acid
Tanning agents, synthetic organic
Tartaric acid and metallic salts
Tartrates
Tear gas
Terpineol
Tert-butylated bis (p-phenoxyphenyl) ether fluid
Tetrachloroethylene
Tetraethyl lead
Thioglycolic acid, for permanent wave lotions
Trichloroethylene

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281 INDUSTRIAL INORGANIC AND ORGANIC CHEMICALS—Continued

2818 Industrial Organic Chemicals, Not Elsewhere Classified—Continued

Trichloroethylene stabilized, degreasing
Trichlorophenoxyacetic acid
Trichlorotrifluoroethane tetrachlorodifluoroethane isopropyl alcohol
Tricresyl phosphate
Tridecyl alcohol
Trimethyltrithiophosphite (rocket propellants)
Triphenyl phosphate
Urea
Vanillin, synthetic
Vinyl acetate

2819 Industrial Inorganic Chemicals, Not Elsewhere Classified

Establishments primarily engaged in manufacturing industrial inorganic chemicals, not elsewhere classified. Important products of this industry include inorganic salts of sodium (excluding refined sodium chloride), potassium, aluminum, calcium, chromium, magnesium, mercury, nickel, silver, tin; inorganic compounds such as alums, calcium carbide, hydrogen peroxide, phosphates, sodium silicate, ammonia compounds and anhydrous ammonia; rare earth metal salts and elemental bromine, fluorine, iodine, phosphorus, and alkali metals (sodium, potassium, lithium, etc.) Establishments primarily engaged in mining, milling, or otherwise preparing natural potassium, sodium, or boron compounds (other than common salt) are classified in Industry 1474.

Activated carbon and charcoal
Alkali metals
Alumina
Aluminum chloride
Aluminum compounds
Aluminum hydroxide (alumina trihydrate)
Aluminum oxide
Aluminum sulfate
Alums
Ammonia alum
Ammonia liquor
Ammonium chloride, hydroxide, and molybdate
Ammonium compounds
Ammonium perchlorate
Ammonium thiosulfate
Anhydrous ammonia
Anhydrous nitrogen tetroxide
Aqua ammonia, made in ammonia plants
Barium compounds
Beryllium oxide
Bleaches, household: liquid or dry
Bleaching powder
Borax (sodium tetraborate)
Boric acid
Boron compounds, not produced at mines
Borosilicate
Brine
Bromine, elemental
Caesium metal
Calcium carbide, chloride, and hypochlorite
Calcium compounds, inorganic
Calcium metal
Calomel
Carbide
Catalysts, chemical
Cerium salts
Charcoal, activated
Chemical catalysts
Chlorosulfonic acid
Chromates and bichromates
Chromic acid
Chromium compounds, inorganic
Chromium salts
Cobalt chloride
Cobalt 60 (radioactive)
Cobalt sulfate
Copper chloride
Copper iodide and oxide
Copper sulfate
Cyanides
Desiccants, activated: silica gel
Diammonium phosphate
Dichromates
Ferric chloride
Ferrocyanides
Fissionable material production
Fluorine, elemental
Fuel propellants, solid, inorganic
Fuels, high energy, inorganic
Getters
Glauber's salt
Heavy water
High purity grade chemicals, inorganic: refined from technical grades
Household bleaches, dry or liquid
Hydrated alumina silicate powder
Hydrochloric acid
Hydrocyanic acid
Hydrofluoric acid
Hydrogen peroxide
Hydrogen sulfide
Hydrosulfites
Hypophosphites
Indium chloride
Inorganic acids
Iodides
Iodine, elemental
Iodine, resublimed
Iron sulphate
Isotopes, radioactive
Laboratory chemicals, inorganic
Lead oxides, other than pigments
Lead silicate
Lime bleaching compounds
Lithium compounds
Lithium metal
Magnesium carbonate
Magnesium chloride
Magnesium compounds, inorganic
Manganese dioxide powder, synthetic
Mercury chlorides (calomel, corrosive sublimate), except U.S.P.
Mercury compounds, inorganic
Mercury oxides
Mercury, redistilled
Metals, liquid
Mixed acid
Muriate of potash, not produced at mines
Nickel ammonium sulfate
Nickel carbonate
Nickel compounds, inorganic
Nickel sulfate
Nitric acid
Nuclear cores, inorganic
Nuclear fuel reactor cores, inorganic

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281 INDUSTRIAL INORGANIC AND ORGANIC CHEMICALS—Continued

2819 Industrial Inorganic Chemicals, Not Elsewhere Classified—Continued

Nuclear fuel scrap reprocessing
Oleum (fuming sulfuric acid)
Oxydation catalyst made from porcelain
Perchloric acid
Phosphates, except defluorinated
Peroxides, inorganic
Phosphoric acid
Phosphorus and phosphorus oxychloride
Potash alum
Potassium aluminum sulfate
Potassium bichromate and chromate
Potassium bromide
Potassium chlorate
Potassium chloride and cyanide
Potassium compounds, inorganic, except potassium hydroxide and carbonate
Potassium cyanide
Potassium hypochlorate
Potassium iodide
Potassium metal
Potassium nitrate and sulfate
Potassium permanganate
Propellants for missiles, solid, inorganic
Radium chloride
Radium luminous compounds
Rare earth metal salts
Reagent grade chemicals, inorganic: refined from technical grades
Refrigerants, ammonia type
Rubidium metal
Salt cake (sodium sulfate)
Salts of rare earth metals
Scandium
Silica, amorphous
Silica gel
Silicofluorides
Silver bromide, chloride, and nitrate
Silver compounds, inorganic
Soda alum
Sodium aluminate
Sodium aluminum sulfate
Sodium antimoniate
Sodium bichromate and chromate
Sodium borates
Sodium borohydride
Sodium bromide, not produced at mines
Sodium chlorate
Sodium compounds, inorganic
Sodium cyanide
Sodium hydrosulfite
Sodium hypochlorite
Sodium, metallic
Sodium molybdate
Sodium perborate
Sodium peroxide
Sodium phosphate
Sodium polyphosphate
Sodium silicate
Sodium silicofluoride
Sodium stannate
Sodium sulfate--bulk or tablets
Sodium tetraborate, not produced at mines
Sodium thiosulfate
Sodium tungstate
Sodium uranate
Solid fuel propellants, inorganic
Stannic and stannous chloride
Strontium carbonate, precipitated, and oxide
Strontium nitrate
Sublimate, corrosive
Sulfate of potash and potash magnesia, not produced at mines
Sulfides and sulfites
Sulfocyanides
Sulfur chloride
Sulfur dioxide
Sulfur hexafluoride gas
Sulfur, recovered or refined, except from sour gas
Sulfuric acid
Tanning agents, synthetic inorganic
Thiocyanates, inorganic
Tin chloride
Tin compounds, inorganic
Tin oxide
Tin salts
Uranium slug, radioactive
Water glass
Zinc chloride

282 PLASTICS MATERIALS AND SYNTHETIC RESINS, SYNTHETIC RUBBER, SYNTHETIC AND OTHER MAN-MADE FIBERS, EXCEPT GLASS

This group includes chemical establishments primarily engaged in manufacturing plastics materials and synthetic resins, synthetic rubbers, and cellulosic and man-made organic fibers. Establishments primarily engaged in the manufacture of rubber products, and those primarily engaged in the fabrication of miscellaneous plastics products, are classified in Major Group 30; and textile mills primarily engaged in throwing, spinning, weaving, or knitting textile products from manufactured fibers are classified in Major Group 22.

2821 Plastics Materials, Synthetic Resins, and Nonvulcanizable Elastomers

Establishments primarily engaged in manufacturing synthetic resins, plastics materials, and nonvulcanizable elastomers. Important products of this industry include: cellulose plastic materials; phenolic and other tar acid resins; urea and melamine resins; vinyl resins; styrene resins; alkyd resins; acrylic resins; polyethylene resins; polypropylene resins; rosin modified resins; coumarone-indene and petroleum polymer resins; and miscellaneous

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